

## SUPPLEMENT TO "CURRENT SCIENCE".

Vol. VI]

October 1937

[No. 4

### The Chemical Effects of Electrical Discharge.

By K. R. Dixit,  
Gujarat College, Ahmedabad.

(Received June 5, 1937.)

#### INTRODUCTION.

THE fact that chemical action accompanies various types of electrical discharge in gases has been known for a long time. Bertholet<sup>1</sup> summarised and reviewed the earlier as well as his own work, in which the arc, spark or silent discharges were applied to a large number of gases and gaseous mixtures. At that time little or no attempt was made to find a general mechanism or theory. This seems but natural if we remember that almost nothing of our present ideas of discharge in gases was known to Bertholet and his contemporaries. Most of their experimental results have, nevertheless, been confirmed by later work.

After the War, classical physics gradually began to change its costume, and dress up as quantum physics. Haber and Zisch<sup>2</sup> observed the emission of light during certain chemical reactions. It was but natural to investigate the reciprocal processes, in which the excited and ionised atoms and molecules produce chemical changes. A summary of the work done upto 1925 is published by Kallmann.<sup>3</sup> He considers the collisions of electrons, ions and neutral atoms and molecules with one another, and also the chemical reactions due to these collisions.

Chemical changes brought about through the agency of an electric discharge, have

been the subject of considerable investigation.<sup>4-15</sup> To-day we regard the chemical change as the change in the electronic configuration of the atom or molecule. In the study of the chemical effects of electrical discharge, these changes in the electronic configuration are brought about through the agency of the electrical discharge. Thus in order to get a physical picture of the whole process, a complete knowledge of the phenomena of electrical discharge becomes absolutely necessary.

#### ELECTRICAL DISCHARGE IN GASES.<sup>16, 17, 18</sup>

Of all the new phenomena wherewith the world has been enriched by modern

<sup>4</sup> Wood, *Phil. Mag.*, 1921, **42**, 729.

<sup>5</sup> Anderson, *Zeit. f. Phys.*, 1922, **10**, 54.

<sup>6</sup> Guntherschulze, *Zeit. f. Elektrochemie*, 1924, **30**, 386.

<sup>7</sup> Balasse, *Bull. Sci. Acad. Roy. Belg.*, 1926, (5), **12**, 193, 835.

<sup>8</sup> Bhatnagar, *Jour. Ind. Chem. Soc.*, 1928, **5**, 379.

<sup>9</sup> Glocker, *Jour. Amer. Chem. Soc.*, 1928, **50**, 1767.

<sup>10</sup> Brewer and Westhaver, *Jour. Phys. Chem.*, a series of papers beginning with 1929, **33**, 883.

<sup>11</sup> Harkins and Gans, *Jour. Amer. Chem. Soc.*, 1930, **52**, 5165.

<sup>12</sup> E. Brinker and others, *Helv. Chim. Acta*, a series of papers beginning with 1929, **12**, 881.

<sup>13</sup> F. M. Penning, *Zeit. f. Phys.*, 1931, **72**, 338.

<sup>14</sup> M. Laporte, *Jour. Chim. Phys.*, 1931, **28**, 655.

<sup>15</sup> And many others too numerous to mention. For detailed references please see *Physikalische Berichte*, **5**, **6**.

<sup>16</sup> *Electrical Phenomena in Gases*, 1932, K. K. Darrow, London.

<sup>17</sup> J. J. and G. P. Thomson, *Conduction of Electricity through Gases*, 3rd Edition, Cambridge.

<sup>18</sup> R. Seeliger, *Physik der Gasentladungen*, Leipzig, 1931.

<sup>1</sup> Bertholet, *Essai de Mécanique* (Dunod, Paris, 1879).

<sup>2</sup> Haber and Zisch, *Zeit. f. Phys.*, 1922, **9**, 302.

<sup>3</sup> H. Kallmann, *Naturwissen.*, 1926, **14**, 427-31.

physics, there is none more beautiful than the glow in a suitably rarefied gas. In the tube between the electrodes, the 'viewless air' takes form and colour, it seems to condense into luminous mists, to gather itself into islands of variously tinted cloud, which zones of darkness divide. So long as the discharge is constant, they keep their places fixed and changeless. The hues are different according to the gas; and as the pressure falls, the contrasts of the light zones and the dark become less sharp, some of the zones expand and crowd the others off the scene. Attracted by the sight the physicists forged onward to lower and ever lower pressures as fast as better pumps were made. Ultimately, the glory of luminous clouds was gone; but now clear cut beams of radiation were visible in the tube: One proceeding from the cathode into the zone of the discharge, other in the opposite sense through openings drilled in the cathode, and a radiation arising from the places where the beam first mentioned hit the wall or any other solid obstacle. So came about the discovery of the electrons, the Canal rays and the X-rays.

The phenomena at lowest densities of gas being so intelligible, it seemed that those at medium densities would be the next to yield their secrets. But the secrets of the glow are well concealed. Systematic studies of the visual appearance of the glow as it varies under wisely-chosen variations of the current, the pressure, and the nature of the gas, have been made, but they are so hard to interpret in any useful way.

I should now describe the appearance of a typical glow at medium pressure, say a millimetre of mercury. Starting from the cathode there is a thin layer of luminosity spread over its surface; next to this there is a comparatively dark space called the 'Crookes dark space' (or the 'cathode or Hittorf dark space'), the width of this depends on the pressure of the gas, increasing as the pressure diminishes. In the Crookes dark space there is a strong positive space charge, and even to the unaided eye it presents a gradation of brightness. Next to this comes one of the luminous mists, the 'negative glow'. This fades off gradually in the second zone of dimness the 'Faraday dark space'; the length

of the Faraday dark space is variable even when the pressure is constant. Beyond this again there is a luminous column reaching right up to the anode and called the positive column; when the current and pressure are within certain limits this column exhibits remarkable alternations of dark and light spaces, these are called striations. In long tubes the positive column constitutes by far the greater part of the discharge, as the length of the positive column alone increases as the length of the tube increases. The negative glow and the positive column are examples of plasma. The field strength in each is low and nearly uniform, this means that the positive and negative charges are nearly balanced. The balance is most nearly perfect in the unstriated positive column; when there are striated positive charge is in excess in a certain part of each and the negative in a certain other part.

The chemical effects of electrical discharge have been studied for all the various forms of the discharge. Thus the chemical effects of the arc, the spark, the glow, the corona and the silent discharges have been studied. However, the same effects can be produced more conveniently by means of a high frequency discharge in a gas enclosed in a chamber. One may attach the terminals of a generator to electrodes immersed in the gas or attach them to electrodes outside, such as ribbons of tin foil encircling the tube or simply put the container of the gas into a solenoid which is traversed by an alternating electric current. In its visible aspect, the high frequency discharge between electrodes resembles a pair of ordinary glow discharges placed end to end, stretching opposite ways from a common positive column midway between the two electrodes; between this central column and either electrode a Faraday dark space, a negative glow and a Crookes dark space are recognisable. It looks as if that the gas is not aware that each electrode is alternately anode and cathode, but disposed itself as though each were permanently a cathode and there were an anode in the centre. When the discharge is evoked by placing the tube within a solenoid, there is not merely the alternating electric field due to the alternating p.d. between the ends of the coil, but another due to the variation of the magnetic field of the current flowing along

the wire. Under the action of this electromagnetic field the discharge sometimes assumes the form of a very brilliant ring whose plane is normal to the axis of the solenoid. On this account the terms 'electrodeless discharge' and 'ring discharge' are often used as if they were synonyms, even in cases where there is nothing resembling a ring at all.

The gas in a discharge tube is in a state remarkably different from its normal tranquil condition. It is luminous, it is chemically active, whatever solid object touches it is hot, on analysis by appropriate ways, it is found to be pervaded by charged fragments of disrupted atoms, free electrons and positive ions; atoms neutral but in abnormal states abound in it; electrical potential and field strength vary in peculiar ways from place to place. A tranquil non-conductive gas consists of molecules or atoms which are electrically neutral. Thus it seems but natural to attribute the peculiar behaviour of a conducting gas to the presence of charged and excited particles. The excited atoms, electrons and positive ions appear in an interesting rôle; they appear, they produce other charged and excited particles and are finally neutralised or transformed to their normal state. For the discharge at very low pressures or the free electron discharge the theory is relatively competent but the data few, while for the discharge at low pressures or the ionic discharge the data are abundant but the theory is defective.

#### THE THEORIES OF CHEMICAL CHANGE.

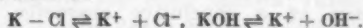
So far we have considered the nature of the electrical discharge, characteristic of the processes, we come across in our subject. We have also seen that a chemical change is essentially a change in the outer electron configuration of the particle which undergoes the change. However, for a better understanding of the subject it is helpful to recollect the historical development of our ideas of the nature of the chemical change.

The earliest<sup>10</sup> general theories of chemical change were dualistic, and electrochemical in character, since they were based mainly upon the properties of inorganic substances in general and of electrolytes in particular.

Valency was thought of exclusively in terms of bonds and no clear distinction was drawn between the structures of such unlike substances as the alcohols and alkalis or the esters and salts, since these were represented by symbols of identical type



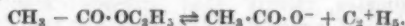
An important advance was made by Arrhenius in 1883, he developed the theory of reversible ionisation as expressed by equations such as



Although, the quantitative aspects of the theory have been shown to be wrong, at least in the case of strong electrolytes, real importance still attaches to the general conception that the covalent molecules may be resolved into ions. The Arrhenius' conception of reversible ionisation is perfectly correct, when applied, for instance, to the salts of mercury



The extension of these ideas to typical organic compounds was made by Euler and Lapworth in 1899.



They supposed that the catalysts acted by increasing the velocity of ionisation, rather than by displacing the position of equilibrium in this balanced action. At the present, the simple ionic mechanism he suggested has been superseded by one according to which the ester first becomes associated with a hydrogen or hydroxyl ion, on the one hand and with a molecule of water on the other; the complex thus formed then undergoes a sort of ionic dissociation, in the course of which an ionic or unsymmetrical fission of the bond between carbon and oxygen leads to the resolution of the ester into acid and alcohol, and at the same time liberates a hydrogen or hydroxyl ion for further service as a catalyst.

The development of the electronic theory of valency has contributed largely to the popularity of the ionic mechanism of organic reactions by providing a clear picture of the conversion of a covalence into an electrovalence as depending on a one-sided distribution of the two shared electrons of a ruptured bond, a reversal of the process whereby the dative bond of Menzies (or the co-ordinate link of Sidgwick) is formed by sharing two electrons belonging originally to

<sup>10</sup> T. M. Lowry, *Trans. Farad. Soc.*, 1934, 30, 3-9.

a single atom, molecule or ion. Thus Brewer and Westhaver<sup>10</sup> (as we shall see later) in the synthesis of  $\text{NH}_3$  and other gases in the glow discharge, found definite evidence that the chemical reaction is due to the formation of positive ions.

There is also a second mechanism whereby organic reactions can proceed, namely that in which a molecule is resolved into two electrically neutral radicals. The work of many physical chemists has brought forth evidence of a conclusive character, this evidence shows very clearly that there are many organic reactions in which the chemical change proceeds through the formation of neutral radicals. Direct evidence of the non-ionic fission of molecules was provided in the first instance from the study of gases. Thus it was shown that iodine-vapour has no marked electrical conductivity at high temperatures, when its vapour density has fallen to one-half the normal value for molecules of  $\text{I}_2$ , these molecules must have therefore dissociated into neutral atoms and not oppositely-charged-ions. The work of Bodenstein, Berthoud, Hinshelwood, and Norrish, indicates clearly that gaseous reactions normally proceed in this way and that ionic reactions are the exception and not the rule so far as gases are concerned. K. K. Darrow<sup>15</sup> goes even further to assert, that the excited atoms or molecules in excited states possessing disposable energy, are mainly responsible for the light, and the chemical action (if there is any) of the discharge. We may say that the success of applying quantum theory in various directions, especially to photochemistry, has led to the belief that although the chemical effect of discharge is proportional to the ionisation, it must, however, be directly caused by excited rather than by ionised molecules. We may further observe, that ionisation itself represents a wholly quantised as well as highly energised state, and that there is every reason to believe that the ions are equally if not more chemically reactive than the excited molecules. On account of the higher electrical field of the ions, their sphere of influence is necessarily larger than that of the excited atom.

The electronic theory has not only provided a clear picture of the resolution of molecules into ions, by the unsymmetrical distribution of the shared electrons of a bond, but with complete impartiality has provided an equally clear picture of the

resolution of a molecule into free radicals by the symmetrical rupture of a bond, in which the two shared electrons are distributed equally between the two atoms which they formerly united. The electronic theory has therefore given precision, not only to the view that there are two types of valency, depending on electron-transfer and electron-sharing, but also to the view that there are two ways in which molecules may undergo chemical change, namely, (i) by the symmetrical rupture of a bond with formation of two neutral uncharged radicals and (ii) by the unsymmetrical rupture of a bond, with the formation of two oppositely charged ions or in the case of a multiple bond (where only one link is ruptured) of a bipolar molecule or pair of bound ions.

#### EXPERIMENTAL INVESTIGATIONS.

The chemical effects of electrical discharge have been investigated for the spark and the arc discharge, for the glow and the corona discharge, and for the silent and the electrodeless discharge. In spite of the host of investigations made during the course of the last 40 years, employing the electrical discharge, where every effort was made to keep the conditions as simple as possible and to exercise all available control over the few variables which are tractable, we still have to deal with a veritable Walpurgisnacht<sup>20</sup> set of phenomena and as is proper to such an occasion, almost anything may be expected to happen. This is especially the case as regards the genesis of molecular species for whose independent existence the older theories of chemistry and physics made no provision. To quote only at random we may mention the formation of metallic compounds of noble gases in the positive column of the glow discharge. The great majority of these quasi-molecules are in the highest degree transitory and representing either positive ions or excited states, have life periods of not more than ca.  $10^{-8}$  second. Fortunately, we can detect these quasi-molecules spectroscopically. The usual methods used in examining the properties of these molecular types formed in the discharge are :—

- (1) The spectroscopic method.
- (2) The measurement of the variation of the pressure of the gas. The pressure at a

<sup>20</sup> Willey, *ibid.*, 1934, 30, 230-45.



given temperature depends on the number of particles present.

(3) To measure the energies of the dissociation of the products formed by the electron impact.

(4) To determine the ratio M/N the chemical yield per ion-pair. M being the number of molecules reacting for N ion-pairs produced.

(5) If the life of the molecules is long enough they can be withdrawn from the discharge and their properties investigated.

(6) Removing the back reaction by freezing out the molecules like  $\text{NH}_3$  as fast as they are formed by a suitable freezing mixture like liquid air or solid  $\text{CO}_2$  and acetone.

#### (1) THE SPECTROSCOPIC METHOD.

(a) *The electrodeless discharge in benzene vapour.*<sup>21</sup>—The electrodeless discharge is a convenient means of effecting the polymerisation or condensation of organic compounds. Thus when benzene vapour at a pressure of 0.1 mm. is subjected to the electrodeless discharge, a greenish white, ring-like glow appears, concentric with and adjacent to the coil of wire which supports the discharge. This glow immediately spreads through the entire vessel, and is extinguished in a red flash; at this stage the benzene is converted into a solid and the pressure becomes too low to carry the discharge. If, however, the benzene vapour is admitted at the proper pressure, the discharge persists as a brilliant white ball, and a brown solid deposits on the walls of the vessel. The formula of this product is  $(\text{CH})_x$ . The spectrum of the discharge shows that the benzene is first decomposed into neutral hydrogen and carbon atoms, with singly charged carbon ions  $\text{C}^+$  and molecules of carbon  $\text{C}_2$  and also  $\text{CH}$  monohydrocarbon. Other organic substances form similar compounds and give related spectra; forming hydroxyl  $\text{OH}$ , cyanogen  $\text{CN}$ , nitrogen  $\text{N}_2$ , singly charged  $\text{N}_2^+$  ions and imine  $\text{NH}$  molecules. In general these atoms, molecules and ions react with each other very rapidly, almost instantaneously, to form products of higher molecular weight. For example, benzene is decomposed and the fragments unite to form a reddish-brown solid almost as rapidly as benzene vapour

can flow into the flask at the proper reduced pressure. One exception is  $\text{H}_2\text{O}$ , which is relatively inactive, and does not seem to unite to any very great extent with the other materials.

Even at the risk of repetition, I should say again, that if any organic gas or vapour is used to carry an electrical discharge, of the type of electrodeless or glow discharge, diatomic molecules are formed. These are revealed by the band spectra which they produce. The bands are most prominent in the visible spectrum, but are also numerous in the ultra-violet region. In addition certain atomic and ionic spectra are more or less prominent. Thus benzene acetylene or any other compound of the general formula  $(\text{CH})_x$ , gives spectra which show that the molecules, presumably by electron impact, are decomposed into  $\text{H}$ ,  $\text{C}$ ,  $\text{C}^+$ ,  $\text{C}_2$  and  $\text{CH}$ . These unite with each other very rapidly to form molecules of very high molecular weight of the same general formula  $(\text{CH})_x$  in the electrodeless discharge, but with a slight deficiency of hydrogen when produced in the glow discharge they unite to form  $(\text{C}_{1-20}\text{H}_{0-30})_x$ . As produced by the electrodeless discharge the solid flakes are of a reddish brown colour, while the glow discharge gives solid substances of various colours, such as brown, white, black together with some liquid material.

It is probable that the energy of the electron impact is the most important factor in smashing of the molecule into the free radicals, ions, etc., formed in the discharge. There must be many positive ion impacts, but they are relatively ineffective, until they acquire velocities comparable to the electron velocities required to produce dissociation or ionisation. Collisions of the second kind also play an important part in the reaction. The fact that in the glow discharge the rate of reaction is most rapid, and that one of the most intense portions of the spectrum is located at the edge of the negative glow, where the density of the high velocity electrons is the greatest, confirms the importance of electron impacts in the reaction. Inner absorption of radiation is also a factor but of unknown importance. Harkins<sup>22</sup> believes that his work indicates that the effects of free atoms and radicals, together with those of ions, are sufficient to explain what occurs.

<sup>21</sup> Harkins and Gans, *Jour. Amer. Chem. Soc.* 1930, 52, 5103.

<sup>22</sup> Harkins, *Trans. Farad. Soc.*, 1934, 30, 221.

(b) *Other similar reactions.*—For the sake of comparison, I should like to mention that in certain respects the conditions in low voltage discharge resemble those in flames, although the velocities of the free electrons in the discharge are usually greater than those of the free electrons in flames. In flames produced by the combustion of organic hydrogen compounds in oxygen, molecules of water, of hydroxyl, of carbon and of carbon monoxide are present. These molecules also exist in electrical discharges which pass through organic vapours, provided these contain the elements oxygen

and hydrogen as constituents. In flames, however, an excess of oxygen converts the carbon partly into carbon dioxide, in electrical discharges in pure organic vapours such an excess of oxygen is not present, so that practically no  $\text{CO}_2$  is formed, carbon and oxygen are combined almost entirely as CO.

Tables I and II originally compiled by Harkins<sup>22</sup> give a short summary of the phenomena observed in the electrodeless and the glow discharge. These tables are quite simple to understand and no explanation seems to be necessary.

TABLE I.  
*Electrodeless discharge.*

Substance	Colour of discharge		Maximum pressure 1.5 cm. gap	Colour of product	Form of product	Rate of formation of product gm. per hour
	Ring	Glow				
Xylene	Greenish-white	White to red	0.26 mm.	Light brown	Powder and scales	1.0
Mesitylene	Do.	Do.	0.30 mm.	Do.	Do.	0.8
Methane	Do.	Do.	1.01 mm.	Do.	Scales	0.0
Pyridine	Greenish-blue	Bluish-white to brown	0.28 mm.	Dark brown	Powder and scales	1.8
Benzaldehyde	Do.	Blue and red to red	0.37 mm.	Do.	Do.	1.2
Thiophene	Intense green	Purple to red	0.19 mm.	Dark brown to black	Some powder and heavy scales	0.7

TABLE II.  
*Glow discharge.*

Substance	Colour of discharge	Colour of product	Form of product	P.D. in volts	Rate of formation of product gm. per hour	Moles per equivalent of current	Molecule per quantum of radiation
Benzene	Blue green to white	Black to yellow	Powder and gum	800	0.5	9.87	102
n-Heptane	Blue green to pink	Black to brown	Powder	800	0.15	2.47	25.5
Methane	Do.	Do.	Do.	450 to 650	0.03	3.28	38.2
Pyridine	Blue to violet	Do.	Powder and scales	800	0.14	2.75	..
Phenol	Blue-green	Do.	Do.	650	0.16	2.40	..

(c) *The free radicals.*—A free radical is a molecule in such a peculiar high energy state, with reference to its union with a like or unlike radical, as to be difficult to isolate it under ordinary conditions. Harkins observed that the free radicals  $\text{HO}$ ,  $\text{CH}$ ,  $\text{NH}$ ,  $\text{C}_2$ ,  $\text{CN}$  and  $\text{CS}$  were present in discharges through various organic vapours. The physical evidence for the existence of the free radicals of relatively short life is largely spectroscopic in character, since free radicals give rise to band spectra with a characteristic fine structure in gases or vapours. The existence of free radicals under less placid conditions may also be disclosed by means of emission spectra consisting of bands instead of lines, e.g., the 'Swan bands' of carbon, the 'steam bands' of Living and Dewar or the 'Schuster bands' of ammonia.

(d) *Active Nitrogen.*<sup>23</sup>—In 1900 E. P. Lewis observed that nitrogen could be stimulated by an electrical discharge to emit a bright yellow glow, which continued for some time after the discharge had ceased; he made a number of spectroscopic observations on the glowing nitrogen. The Lord Rayleigh investigated the phenomena in a more general and systematic manner, and discovered that the 'glowing gas' had remarkable chemical properties and named it 'active' nitrogen. Certain important conditions must be observed for the production. The pressure of  $\text{N}_2$  must be a few millimetres of mercury, at higher pressures collisions with ordinary  $\text{N}_2$  molecules apparently destroy the glowing substance. The best procedure is to draw a stream of rarefied  $\text{N}_2$  through the discharge tube by means of a pump. The persistence and gradual decay of the glow in the gas which has left the region of the discharge can be easily observed. When the discharge is from an induction coil, it should be a condensed discharge, the use of the condenser giving a sudden intense current.

At first it was thought that a little oxygen must be present but methane,  $\text{H}_2\text{S}$ , ethylene and various other substances are equally efficacious. It seems that a trace of some electro-negative gas, i.e., a gas which readily takes up electrons, to give negative ions is the essential thing. A few parts per 1000 of the foreign gas produce the most intense glow, larger amounts destroy it. The glowing nitrogen was shown by Rayleigh to have

great chemical reactivity and also to excite many substances to luminescence. It reacts with acetylene to give hydrogen cyanide, and with mercury to give nitride, mixed with iodine-vapour it produces a brilliant blue light.  $\text{H}_2$  and inert gases merely dilute the glow, but  $\text{O}_2$  extinguishes it altogether. It interacts with nitric oxide with the production of a greenish flame, the evolution of heat, and the formation of nitrogen peroxides and nitrogen.

Although the production of the glow is determined by the presence of other gases, apparently, the actual emission process is one in which  $\text{N}_2$  alone is concerned, for the spectrum is identical whether the impurity is  $\text{O}_2$ , methane or  $\text{H}_2\text{S}$ . The glow is not associated with any form of ionic  $\text{N}_2$ ; it is unaffected by the removal of ions from the gas which has passed through the discharge. Moreover, the most important group of bands observed is the well-known group of 'first positive' bands; and the spectroscopic evidence goes to show that the first positive bands of  $\text{N}_2$  are emitted by the neutral molecule itself. It therefore seems fairly certain, that the characteristic luminescence is emitted by simple diatomic  $\text{N}_2$  in some unusual stage.

We now come to the question of the mechanism by which these active molecules are produced and decay. It has been suggested that, in the discharge, free atoms of nitrogen are produced, in a manner analogous to that in which Wood's atomic hydrogen is formed. These have to give rise to a molecular spectrum, which they can do in two ways, either by simple recombination, or by the communication of the energy of recombination to a normal nitrogen molecule, which collides with the two atoms at the moment of their union. We thus have three possible views:—

(a) Molecules of nitrogen excited in the discharge to a high energy level are metastable, i.e., they have a considerable life and can continue to exist for some time after leaving the discharge, when they slowly revert with the emission of light.

(b) Atomic nitrogen emerges from the discharge, and then recombination takes place to give the molecules which are at a high enough energy level to emit the spectrum.

<sup>23</sup> Hinshelwood, *Nature*, 1928, 122, 404.

(c) Nitrogen atoms emerge from the discharge and cause excitation of normal molecules in the ternary collision ( $2\text{N} + \text{N}_2$ ).

Ordinarily an excited molecule loses its energy in  $10^{-10}$  second and no independent evidence of the metastable states as assumed in (a) exists. Free atoms cannot combine as assumed in (b) unless they suffer a collision with a third molecule which can remove the excess energy liberated in their union. Thus (c) becomes a natural hypothesis to make, the third body being  $\text{N}_2$  which is excited to luminescence in the process. If this is the case, the rate of decay should be directly proportional to the total pressure of ordinary  $\text{N}_2$ . The opinion on this point is somewhat divided.

It remains now to consider the part played by the small proportion of foreign electro-negative gases in the production of active nitrogen, we have seen that the impurities play no part in the actual light emission process. Their function must, therefore, be in some way to catalyse the formation of the atoms on the excited molecules in the discharge (which is unlikely), or to retard the spontaneous reversion of the active nitrogen, which in their absence may be very rapid indeed, or take place by some process not attended with luminescence.

The electrical discharge in gases like hydrogen, oxygen and chlorine gives us active hydrogen,<sup>24,25</sup> active oxygen<sup>26</sup> and active chlorine.<sup>27</sup> These gases however appear to show chemical activity as a consequence of their atomic character. It is possible to obtain the atoms of these gases in considerable quantities. Schwab and Friess obtained the spectrum of the discharge through chlorine. They estimate the average life of a chlorine atom, in their experiments, to be about  $3 \times 10^{-3}$  seconds.

## (2) THE MEASUREMENT OF PRESSURE.

The pressure of a gas at a given temperature depends on the particles present, thus the measurement of the change of pressure

would give us an idea as to the relative change in the number of particles. If the change produced by the discharge is comparatively simple, the relative variation of pressure may enable us to guess and verify the reactions taking place. Hutchison and Hinshelwood<sup>28</sup> used this method to compare the rates at which two reactions—thermal and photochemical—take place in a discharge tube; and to see whether the results agreed in a general way with what might be expected from the known thermal reactions. Nitrous oxide and ammonia were chosen for experiment, the thermal decomposition of nitrous oxide being known to occur much more readily than that of ammonia.

The apparatus used for comparing the stability of the two gases under electrical excitation consists of a discharge tube, connected by a two-way tap to a McLeod gauge and to a series of pipettes whereby it could be filled with gas at any desired pressure. The whole system could be evacuated by a two-stage mercury pump. The current was supplied by a simple induction coil. The course of the reaction was followed by reading the change in pressure on the McLeod gauge. It was first established by a large number of experiments that the absolute amount of decomposition tended to be independent of the initial pressure of the gas when the discharge was feeble, but with increasing intensity of discharge the amount of decomposition became proportional to the initial pressure, i.e., the percentage amount was now independent of the initial pressure. This for obvious reasons, is the condition for a satisfactory comparison, and consequently all measurements were made with discharges sufficiently intense to bring the reaction into this 'unimolecular' region. Values of the 'unimolecular velocity constant' are used for the purposes of tabulation.

Most of the nitrous oxide ultimately decomposes to  $2\text{N}_2 + \text{O}_2$ ; the argument is unaffected by any that decomposes to  $2\text{NO} + \text{N}_2$ , since the volume change is the same. In any case we are using the velocity constants in a purely empirical way.

<sup>24</sup> Wood, *Phil. Mag.*, 1922, 44, 538.

<sup>25</sup> Botheffer, *Zeit. f. Physik. Chem.*, 1924, 113, 199.

<sup>26</sup> Harteck and Kopsch, *ibid.*, 1931, B, 12, 327.

<sup>27</sup> Schwab and Friess, *Zeit. f. Elektrochemie*, 1933, 39, 586.

<sup>28</sup> Hutchison and Hinshelwood, *Proc. Roy. Soc.*, 1928, 117, 131.



Each comparison was made only under those conditions of discharge where previous observation had shown the reaction of each separate gas to be 'unimolecular'. Considering the wide range of conditions under which the four sets of experiments were carried out, Hutchison and Hinshelwood conclude that the ionic impacts required to decompose ammonia are more violent than those required to decompose nitrous oxide. Moreover, the correlation between the greater stability of ammonia in the discharge and its higher thermal energy of activation appear to be very suggestive.

The above detailed description of the experiments carried out by Hutchison and Hinshelwood, shows clearly how such a simple device of observing the change of pressure, can lead to important results, if the necessary precautions are taken.

### (3) THE ENERGIES OF THE DISSOCIATION OF THE PRODUCTS FORMED BY THE ELECTRON IMPACT.<sup>20</sup>

Collisions between the electrons and molecules of a gas produce a number of fascinating phenomena. The results of such collisions are far more complicated than those involved in impact between electrons and atoms, for although the direct action of the projectile electron is doubtless upon the electrons of the molecule just as in atomic impact, the subsequent effects are much more varied. Provided the pressure is sufficiently low an atom, once excited by impact, has little choice but to lose the energy of excitation by radiation. An excited molecule on the other hand may radiate or it may dissociate in a variety of ways. An interesting feature of the dissociating process is that in general the constituents fly apart with considerable velocity. This results from the fact that the electron's action on the molecule is completed before the constituent atoms have changed much in position. Thus when dissociation takes place the act of the projectile electron is so to modify the electron configuration of the molecules that the resultant force between the atoms is repulsive while the atoms are still close together. The consequent effect of this is that the atoms fly

apart, and in doing so attain considerable kinetic energy. If the energy communicated to the molecule by the electron-impact is  $V_i$  and if  $U_2 - U_1$  is the change in the potential energy of the constituent parts of the molecule before and after dissociation, it is readily seen that the energy which appears as kinetic energy of the products of dissociation is  $V_i - (U_2 - U_1)$ , if the masses of the products of dissociation are equal, as in the case of  $H_2$  or  $N_2$  the kinetic energy of each atom after dissociation will be  $\frac{1}{2} [V_i - (U_2 - U_1)]$ . If the masses are unequal and  $m_1$  and  $m_2$  the kinetic energy of the constituent 1 is  $\frac{m_2}{m_1 + m_2} [V_i - (U_2 - U_1)]$ . Experimentally we can measure the minimum energy the electrons need to have ( $V_i$ ) to produce a dissociating product which has the measured energy,  $V_r$ . It is evident that the relation between  $V_r$  and  $V_i$  should be a linear one, that the slope should be  $m_2/(m_1 + m_2)$  and that the intercept on the  $V_i$  axis is the value of  $U_2 - U_1$ .

In the case of each gas measured by Tate and Lozier measurements were directed towards the determination of the following :

(a) The distribution of the kinetic energy among the ions produced by electrons having a specified velocity.

(b) The minimum electron energies necessary to produce an ion of specified energy.

(c) The relative efficiencies of production of ions having a specified energy as a function of the velocity of the incident electrons.

They studied the energies of the dissociation products of  $N_2$  and CO formed by electron impact. They measured the kinetic energy distribution of  $C^+$  ions formed from CO and  $N^+$  ions from  $N_2$ , and found that for both gases the most probable kinetic energy of ions is about 3 volts. They further observed that the minimum electron energies necessary to produce  $C^+$  and  $N^+$  ions of specified energy satisfy the requirements of the principle of conservation of energy. Their results are summarised in Tables III and IV.

TABLE III.

Process	Heat of Dissociation in Volts
$N_2 \rightarrow N + N$	$8.4 \pm 0.5$
$N_2^+ \rightarrow N^+ + N$	$> 7.1 \pm 0.5$
$CO \rightarrow C + O$	$9.3 \pm 0.5$
$CO^+ \rightarrow C^+ + O$	$> 6.4 \pm 0.5$

<sup>20</sup> Tate and Lozier, *Phys. Rev.*, 1932, **39**, 254-69.

TABLE IV.

Probable Process	Energy of Ions in Volts	Energy of Impacting Electrons in Volts
$N_2 \rightarrow N^+ + N + e^-$	2~7	27~37
$N_2 \rightarrow N^+ + N^* + e^-$	1~2	35~37
$N_2 \rightarrow N^+ + N^+ + 2e^-$	4~8	46~54
$CO + e^- \rightarrow C + O^-$	0~1	10~14
$CO \rightarrow C^+ + O^-$	0~2	22~26

## (4) TO DETERMINE THE RATIO M/N.

In this method we determine experimentally the ratio M/N, the chemical yield per ion-pair. Where M is the number of molecules reacting for N ion-pairs produced.

In order<sup>30</sup> to investigate the interaction between the slowly moving ions and the gas molecules, two different methods have been used. The first method may be described as the chemical method. In this method we determine the amount of freshly formed chemical product, and also the total number of ions produced in the reaction, i.e., we try to determine the amount of the newly formed chemical product per ion produced in the reaction. The second method is the method of the molecular or strictly speaking ionic-rays, we shall consider this method in the next section.

Lind<sup>31-34</sup> has carried out a number of investigations by the chemical method. He studied the changes taking place in a gaseous mixture exposed to radium emanation. The measurement of pressure, gave him the chemical composition of the mixture; further the number of ions produced is also known, if the amount of radium emanation present is known. Now Lind investigated the action of the radium emanation on a number of gases and gaseous mixtures and obtained a number of interesting results. For instance he observed that in a mixture of hydrogen and oxygen exposed to emanation, water is produced, and that every ion-pair produced leads to the formation of about four water molecules.

His<sup>35</sup> experiments show that the chemical action produced by  $\alpha$ -rays is not only pro-

portional to, but strictly equivalent to, the ionisation. This equivalent is not equal to the Faraday equivalent, but greater within restricted limits. Since for all  $\alpha$ -ray reactions the value of M/N exceeds unity, usually having values 2 and 20. Lind finds it necessary to assume some kind of multiplying process. Thus we can suppose that during the process of ionisation, we obtain a positively charged molecule and an electron; this positively charged molecule attaches itself, by what may be regarded as Van der Waals' forces, or polarising forces, to neutral gas molecules, thus forming "ion clusters"; these ion clusters finally collide with an electron or a negative ion and are neutralised. During this process of neutralisation, however, the "ion cluster" breaks up into new molecules.

## (5) STABLE AND METASTABLE PRODUCTS.

If the life of the molecules or other particles produced in the discharge is long enough, it becomes feasible to withdraw them from the discharge tube and to investigate their properties. These properties which we can investigate may be physical, chemical or even spectroscopic. This possibility of removing the products of the discharge from the discharge tube, leads us to the method of ionic rays. In this method the ions are produced in a gas, contained in a vessel, the pressure of the gas being about 1/1000 mm. of mercury. Usually, the thermionic electrons are used to produce ionisation. These ions leave the discharge through different slits, in the form of a beam of charged particles. This well-defined beam then passes through an electric and a magnetic field, just as if it were a beam of positive rays. The ratio of the charge to the mass of the ion and the ionic velocities are then determined in the same manner<sup>36, 40</sup> as for the positive rays. This method has already been used for the simple gases<sup>36-38</sup> like  $H_2$ ,  $N_2$  and  $O_2$ . In all these cases the positive ions  $H_2^+$ ,  $N_2^+$  and  $O_2^+$  have been observed to be present. This shows that the electrons produce the same type of ions as were

<sup>30</sup> Kallmann and Dorsch, *Naturwissen.*, 1927, **15**, 788-89.

<sup>31</sup> S. C. Lind, *Jour. Amer. Chem. Soc.*, 1919, **41**, 531.

<sup>32</sup> *Ibid.*, 1923, **45**, 2585.

<sup>33</sup> *Ibid.*, 1924, **46**, 2003.

<sup>34</sup> *Ibid.*, 1925, **47**, 2675.

<sup>35</sup> S. C. Lind, *Science*, 1928, **67**, 565-69.

<sup>36</sup> Smyth, *Phys. Rev.*, 1925, **25**, 452.

<sup>37</sup> Hogness and Lunn, *ibid.*, 1925, **26**, 44 and 786.

<sup>38</sup> Kallmann and Bredig, *Zeit. f. Phys.*, 1925, **34**, 736.

<sup>39</sup> Eisenhut and Conrad, *Zeit. f. Elektrochemie*, 1930, **36**, 654.

<sup>40</sup> Fraser, *Trans. Farad. Soc.*, 1934, **30**, 182.

observed to be produced by Lind by means of  $\alpha$ -rays. This method is very sensitive and the presence of such complex ions like  $H_3^+$  and  $H_2^+$  which form an extremely small fraction of the discharge products can also be detected.

(6) REMOVING THE BACK REACTION BY FREEZING OUT THE MOLECULES FORMED.<sup>40</sup>

In a series of experiments carried out by Brewer and Westhaver, the back reaction was completely removed by freezing out the newly formed products in the discharge tube. The freezing mixture of solid carbon dioxide and acetone or liquid air were used to freeze out the product. Among many others they investigated the synthesis of ammonia, nitrogen dioxide and ozone in the glow discharge.

To get an idea of the method used, let us consider a special case like the synthesis of ammonia in the glow discharge. The synthesis was investigated from 4 mm. to 0.1 mm. pressure of a 3-1 mixture of hydrogen and nitrogen. The discharge tubes used were of two general types, one in which a portion of the positive column was immersed in liquid air, and the other in which the entire tube including the electrodes was immersed. The electrodes were made of aluminium rods or discs clamped to tungsten leads. The exposed tungsten was glass-covered to prevent sputtering. When only the positive column was immersed, tungsten exploring electrodes were sealed into the tube at the liquid air-level. The potential drop through the region of the discharge in which ammonia was being frozen out was measured by an electrostatic voltmeter connected to the exploring electrodes. When the entire tube was immersed, the voltmeter was connected directly to the discharge electrodes. Most of the results were obtained by using a 1 K.W. 20,000 volt transformer for the current supply. The currents through the discharge tube were measured either with an A.C. milliammeter or a vacuum thermocouple and galvanometer. The discharge current was controlled by rheostats in the primary circuit of the transformer. For the D.C. work the transformer was replaced by a 10,000 volt rotary converter.

It was observed that for any particular discharge tube the rate of synthesis is proportional to the current passing through

the discharge and is independent of the pressure and the potential gradient. The rate of synthesis per unit of current and per unit of power was calculated for discharge tubes of various types. The current efficiency varies directly with the length of the column immersed and the power efficiency increases with the bore of the tube. The presence of the magnetic field at right angles to the electric field showed a material increase in the rate of synthesis, while a parallel field did not show any effect. Brewer and Westhaver interpret the data, as showing, that the synthesis is a pure gas reaction, that the reaction is initiated by the positive ions formed in the discharge, and further that the rate of synthesis is proportional to the rate of formation of ions present and hence to the current. They also conclude, that their results appear to suggest a new electro-chemical equivalence law for discharge tubes. This law may be stated as follows: for a given set of operating conditions the rate of synthesis is independent of the pressure and depends only on the current passing through the tube. This may be expressed as  $dP/dt = aI$ , where  $P$  may be defined as the equivalent pressure,  $I$  is the current, and  $a$  is a parameter which depends on the condition of the experiments.

(7) MISCELLANEOUS REACTIONS.

For the sake of completeness I should like to mention here some experiments carried out by Miyamoto<sup>41</sup> and some others of Yajnik, Sharma and Bhatnagar.<sup>42</sup>

Miyamoto used a discharge tube made up of two concentric cylinders, the discharge was allowed to pass through the annular space between the two cylinders. In this annular space fine powders of different salts were placed, the space was then filled with hydrogen and a discharge allowed to pass through it. The gaseous as well as the solid products of the discharge were collected and analysed. About twenty different salts of metals were investigated and it was observed that as a rule they change their character. Similar investigations of Yajnik, Sharma and Bhatnagar also show similar transformations. They observe, however, that phosphates, oxalates

<sup>41</sup> S. Miyamoto, *Jour. Sc. Hiroshima Univ.*, (A), 1932, 2, 217-42.

<sup>42</sup> Y., S. and B., *Zeit. f. Phys. Chem.*, (A), 1930, 148, 394.

and calcium carbonate are comparatively more stable.

#### THE THEORIES OF CHEMICAL ACTION IN ELECTRICAL DISCHARGE.

The chemical action accompanying the various types of electrical discharge, has been observed and studied for the last sixty years. Still no single theory of such chemical reactions has been able to explain all the results experimentally obtained. All that a single theory could explain has been a set of results obtained in one particular type of experiments. In our review of the theories of the chemical reactions, we are thus obliged to consider the various explanations put forward to explain the different sets of results obtained. The most convenient way to study these different explanations is to divide the work done in suitable groups.

The glow discharge tube offers a fertile field for a study of the elementary units initiating chemical action, since within the discharge are to be found electrons, positive ions, neutral particles and excited molecules and atoms. Each of these has been suggested by different investigators as the elementary reacting unit. The theory of the discharge tube is not sufficiently worked out to enable a complete mechanism to be presented, nevertheless, it is possible to offer some highly probable suggestions regarding the nature of the reaction.

Naturally, the first attempts to find a theory for the electro-chemical effects in gases were directed towards a correlation between the current flowing and the amount of action produced according to Faraday's law. Faraday's law states that for monovalent electrolytes, if  $M$  is the number of gram molecules of the electrolyte changed due to the passage of  $F$  Faradays of electricity (1 Faraday = 96540 coulombs), the ratio  $M/F$  is equal to unity. In gases exposed to ordinary ionising agents a very large number of the ions formed is singly charged. Thus monovalent electrolytes may be considered as the electro-chemical analogue of the ionised gas, and we may apply to an ionised gas the Faraday's law for monovalent electrolytes. The ratio of  $M/F$  in this case becomes the ratio of  $M/N$ , where  $M$  is the number of molecules reacting for  $N$  ion-pairs produced. If

Faraday's law can strictly be applied to an ionised gas, the ratio of  $M/N$  must have the value unity. Experimentally however Warburg<sup>43</sup> obtained values varying from 35 to 335. Similar results have been obtained by other workers. The disagreement while unexpected, was so unmistakable that these efforts to explain the electro-chemical effects of gases in terms of the Faraday's law had to be abandoned. The theories advanced since may be classified as follows:—

- (1) The photochemical theory of Warburg.
- (2) The static-ion theory of Lind.
- (3) The ion-cluster theory of Rice.
- (4) The chemical equivalence-law for discharge tubes suggested by Brewer and Westhaver.
- (5) The theory of critical activation by kinetic ions suggested by Donnan.

We shall consider these theories in their respective order. But before I proceed further, I should like to remark that in spite of the above classification, which I have made only for the sake of convenience, I do not want to suggest that the mechanism of reaction in any two groups as mentioned above is entirely different.

#### (1) THE PHOTOCHEMICAL THEORY OF WARBURG.

Upon failing to find a relation between current and chemical effect Warburg quite early adopted the idea that ozone formation, for example, might be due to the ultra-violet light accompanying the discharge. In his review<sup>44</sup> of the subject in 1925 he still adheres to this hypothesis. In this paper he observes that the products of a photochemical action on a gas are identical with the products produced by the action of a silent discharge on the same gas. We explain the photochemical action by assuming that the molecule absorbs a quantum of radiation, this additional energy enables the molecule either to dissociate or to combine with other molecules. Exactly, a similar transformation takes place in the silent electric discharge here, however, the additional energy quantum is derived from a colliding molecule instead of from the radiation.

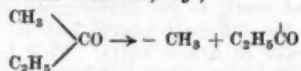
<sup>43</sup> Warburg, *Jahrbuch der Radio und Elek.*, 1909, 6, 181-229.

<sup>44</sup> Warburg, *Zeit. f. Tech. Phys.*, 1925, 6, 625-33.



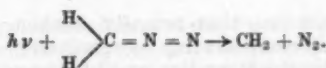
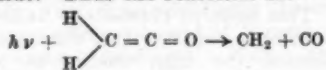
Photochemical theory of Warburg has again come into prominence. This is due to the observation that polyatomic molecules when irradiated by light of a suitable wavelength, split up and give rise to free radicals. Free radicals as already remarked are present in a discharge tube, and their presence has been definitely proved by the spectroscopic methods. Free radicals are produced largely as the decomposition products of polyatomic molecules. A study of the spectroscopic and photochemical properties of polyatomic molecules is capable of yielding information of considerable weight. This information is to be obtained from an interpretation of absorption and fluorescence spectra, and from an analytical examination of the products of the photochemical change and the efficiency of their production.

A close study of the work of Norrish<sup>45</sup> on the photochemical production of some free radicals will give us an idea as to what may be supposed to take place in the discharge tube if we accept the photochemical theory. While studying the photochemical production of radicals Norrish observed that the production of free methyl or ethyl radicals may be achieved photochemically by the irradiation of simple ketones by light of about 2800 A.U. According to him it is the primary change which must involve a liberation of free radicals, *e.g.*,



and that the radicals  $\text{C}_2\text{H}_5\cdot\dot{\text{C}}\text{O}$  and  $\text{CH}_3\cdot\dot{\text{C}}\text{O}$  must decompose spontaneously in order to account for the quantitative formation of carbon monoxide. The free hydrocarbon radicals then combine to give the mixture of hydrocarbons found in practice.

The importance of taking into consideration the energy liberated when free radicals change into stable molecules became strikingly evident to Norrish in his study of the photo-decomposition of diazomethane and ketone both in the vapour state. The results indicate that the primary photochemical change consists in splitting of molecules to give a  $\text{CH}_2$  radical and nitrogen or carbon monoxide. Thus the reactions are



The character of the absorption spectra shows that the primary splitting of the molecule does take place in the above manner.

Many other similar investigations lead Norrish to the following picture of the physical process. It is usually possible to regard the simpler polyatomic molecules as covalent systems in which chemically the individuality of the component atoms has been lost; their outer electronic structures have become as it were fused together into a single system with a new set of properties. Ammonia, carbon dioxide, sulphur dioxide, nitrogen peroxide, benzene and numerous ions can be so regarded. With more complicated substances, however, it is not possible to make this simplification, and in general, the larger polyatomic molecules of organic chemistry have to be regarded rather as an assemblage of covalent groups, each group very largely retaining its individuality within the whole structure and conferring upon the molecule its own specific properties. The individual groups which go to the making of a polyatomic complex have their own spectra, which may be modified by the proximity of the other groups. Light may be absorbed at one bond of the molecule and decomposition occur at another, this fact although it appears rather strange at first is still in harmony with observations on thermal activation.

It is sometimes found that a molecule may be activated in several different ways for the same chemical change. This would be expected if the different activated states corresponded to the different distributions of the energy among the vibrational degrees of freedom, and if there were different probabilities for the transfer of this energy to the bond which must be broken in actual chemical transformation. The experimental discovery of the different activated states seems to show that such internal transfers do in fact occur. Something similar may take place in a photochemical change. In accordance with well-known principles, the excitation of the molecule by light may cause its passage to a new electronic state in which the number of the vibrational quanta is also much higher than in the normal state. It might be the vibrational energy thus indirectly imparted to the molecule which flows from the bond originally

<sup>45</sup> Norrish, *Trans. Farad. Soc.*, 1934, 30, 103-20.

concerned into that actually broken. It is only the compensating reorganisation of the molecule which renders possible the splitting of a particular link. Thus the energies of activation are frequently much smaller than the energy required to break a particular link.

The presence of the free radicals in the discharge tube, and the very clear physical picture given by Norrish, Hinshelwood and others, of the transformations which follow when free radicals are present, lead K. K. Darrow<sup>15</sup> to assert that the excited atoms or molecules in the excited states possessing disposable energy, are mainly responsible for the light, and the chemical action (if there is any) of the discharge. We must, however, remember that on account of the higher electrical field of the ions their sphere of influence is necessarily larger than that of the excited atoms. The ions may therefore be expected to give rise to a few transformations at least; and that we may expect the photochemical mode of transformation as one of the few and not the only mode by which a chemical reaction may be brought about in a discharge tube. This argument is really applicable *mutatis mutandis*, to all the five theories we are considering.

#### (2) THE STATIC-ION THEORY OF LIND.<sup>35</sup>

The equality of ozonization and ionization of oxygen by means of a Tesla discharge convinced Krüger in 1912 of a static-ion theory of ozone formation. At about the same time a study of ozonization under  $\alpha$ -radiation led Lind to the same conclusion. The central hypothesis of the static-ion theory is that the chemical action is the direct result of recombination of positive and negative ions in the bosom of the gas, which never reach the electrodes and hence can have no relation to the current. In fact, this represents in some respects a complete antithesis to the conditions of electrolytic reaction. In electrolysis it is the ions which conduct that react chemically, while in gaseous discharge it is the ions that recombine without conducting that react chemically; possibly the ions which conduct also react chemically at the electrodes, but their number is negligibly small under usual conditions of chemical action in gaseous discharge. In other words, an intensity of ionisation that corresponds to measurable chemical action on a

basis of equivalence is far outside the range in which saturation current can be produced or even approached. Any attempt to attain saturation by applying more voltage simply produces more ionisation by collision, and defeats its purpose by a yet wider margin.

The theory of the electrical discharge is as yet so imperfectly understood, that it is neither possible to measure the total ionisation accompanying an electrical discharge, nor to calculate the ratio of  $M/N$  the chemical yield per ion-pair. In order to be able to calculate the total ionisation Lind used  $\alpha$ -rays as the ionising agent. He observed that the chemical action produced by  $\alpha$ -rays is not only proportional to but is strictly equivalent to, the ionisation. This equivalent is not equal to the Faraday equivalent, but greater within restricted limits. Since for nearly all  $\alpha$ -ray reactions the value of  $M/N$  exceeds unity, and usually lies between 2 and 20, we must assume some kind of multiplying process; which is the same as assuming ion-clusters, for the existence of which there is also some physical evidence.

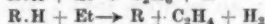
The clustering hypothesis of the mechanism of chemical action produced by gas ions may be stated as follows: When a gas molecule is ionised, one of its electrons is removed, this requires a minimum amount of work to be performed, which is different for different gases, but is usually of the order of a few volts. This leaves a positive ion possessing a large amount of latent energy, and which, owing to its charge, will exert an induced attraction on neutral molecules, thus forming an ion-cluster while still retaining its positive charge. This force of attraction is really due to polarisation of the neutral molecule and is called the Van der Waals force. We do not know precisely the size of these clusters nor the efficiency of collision in clustering, but the chemical  $M/N$  ratios give a minimum—probably a critical value for the portion which we may call the chemical cluster; while the physical cluster may be larger and is probably in dynamic equilibrium with the colliding neutral molecules and hence is rather variable than critical in size. This positive cluster can unite with an electron or a negative ion, during such a neutralisation the high energy of ionisation is set free and the cluster either dissociates to the original components (the energy

being lost as heat) or it may dissociate partly or wholly into elements or into new products of higher heat content or may be largely stabilised to a product of high molecular weight. The heat of ion-recombination is either radiated away or carried off by some of the molecules from the cluster.

In support of the theory we need only consider the effect of electrical discharge on gases like ethane or benzene vapour. Lower hydrocarbons are condensed to higher ones by the elimination of hydrogen or methane, with the formation of some liquid hydrocarbons. The principal feature of Lind's static ion theory thus appears to be, that the ionisation must be the primary step in chemical action under electrical discharge.

### (3) THE ION-CLUSTER THEORY OF RICE.<sup>46, 47, 20</sup>

There seems to be a close parallelism between the electrical decomposition of the simple hydrocarbons and their thermal decomposition, this is of much interest in view of the mechanism proposed by Rice for the thermal processes. According to Rice the aliphatic hydrocarbons decompose in a chain reaction which is induced by the only radicals which are relatively stable like methane and ethane, the general scheme being one or the other of



This can be applied upto  $C_6$  and gives results in fair agreement with those expected upon the assumption of certain arbitrary probabilities of primary, secondary and tertiary C-H bonds being involved. It is a consequence of this theory that if the photochemical decomposition of paraffins and probably hydrocarbons in general proceed through the intermediate formation of free radicals, the quantum efficiency should be large, and the same high yield (M/N ratio) of reactant per unit activating agent should apply to chemical changes induced by  $\alpha$ -particles or the discharge. The apparent applicability of Rice's theory to these electrochemical data seems to have a bearing upon an often debated problem namely the close similarity between the quantum efficiencies and M/N ratio observed in certain reactions. Fair agreement

between calculation and observation has been obtained in both random reactions and those involving a discharge, upon the assumption that clusters, often of five or more molecules are formed either by the process of electrostatic induction round an ion or by action upon dipoles already present, the chemical change taking place upon neutralisation of the charge; and this has naturally led to the suggestion that such a mechanism might be operative in the photochemical process.

It must, however, be stated that very little direct evidence is known for the existence of such ion-clusters. Loeb<sup>48</sup> applying the Debye theory of dielectric constants and the forces on ions in solutions, shows that a cluster of more than 12 molecules should not be stable and that 2 or 3 is a more probable number. There is hardly any spectroscopic evidence for such cluster, while positive ray studies, have also failed to reveal their existence in reactions where, *ex hypothesi*, they should be present. It may be suggested that further knowledge with regard to the reactions of free-radicals may lead to a better understanding of the mechanism of these  $\alpha$ -particle reactions and discharge reactions and *ipso facto* contribute to photochemical theory. It is, however, not yet clear how Rice's hypothesis, taken as an alternative to the ion-cluster postulate can lead to an explanation of polymerisations (conversion of methane to liquid hydrocarbons in the silent discharge at ordinary pressures) or the well-known condensation of acetylene to benzene in various types of discharge. By comparison with the photochemical reactions, we may say, that we have a primary process in the production of free radicals, and the subsequent events are similar to those which immediately follow the absorption of a light quantum, i.e., they are secondary reactions which are naturally variable by conditions of experiment.

### (4) THE CHEMICAL EQUIVALENCE LAW FOR DISCHARGE TUBES SUGGESTED BY BREWER AND WESTHAVER.<sup>10</sup>

Brewer and Westhaver performed a series of experiments in which the freshly formed chemical product was frozen out, thereby removing the back pressure. The

<sup>46</sup> Rice, *Journ. Amer. Chem. Soc.*, 1931, 53, 1959.

<sup>47</sup> Rice, *Trans. Farad. Soc.*, 1934, 30, 152.

<sup>48</sup> Loeb, *Kinetic Theory of Gases*, p. 451 onwards.

state of affairs in the discharge tube may under these circumstances be described as the saturation condition, where no freshly formed product is present. In order to explain their results, they suppose the chemically active species to be positive ions, while the electrons due to their greater mobility carry the current. At saturation, the condition under which they worked, the two positive and negative ion currents are exactly equal and hence the rate of chemical change is proportional to the current. This relation is called by them by the name "the chemical equivalence law" which says that in a glow discharge, the rate of synthesis may be expressed as  $dP/dt = \alpha I$  where  $P$  is the equivalent pressure (e.g., of  $NH_3$  in the  $NH_3$  synthesis),  $I$  the discharge current and  $\alpha$  is a factor that is independent of the actual gas pressure, provided the composition of the gas remains unchanged.

This fact that the rate of synthesis is dependent only on the current and is completely independent of the pressure, led Brewer and Westhaver to conclude that the initial reactants must be positive ions, rather than atoms or excited molecules formed directly in the discharge. Had the reaction been due to excited molecules, the rate should have decreased rapidly with decreasing pressure, and had the reaction been due to atoms, the rate should have increased with increasing pressure. The fact that the initial reactants are ions is again shown in a very conclusive manner by the action of the magnetic field. In the bulb, the field parallel to the plane of the electrodes completely eliminated the general glow throughout the tube, but had no effect on the current nor on the rate of synthesis.

In the synthesis of  $NO_2$  Brewer and Westhaver obtained a maximum yield of about one molecule of  $NO_2$  per electron flowing in the outer circuit. Excess of nitrogen was observed to increase the reaction rate over a large composition range, excess oxygen always retards the rate, excess helium has no effect on the reaction rate for gas mixtures containing less than 70% helium, while argon has a pronounced retarding action. The interpretation of these facts is according to them as follows: The formation of  $NO_2$  is initiated entirely by the positive ions formed in the discharge, which are probably  $N_2^+$  ions, as the addition of excess nitrogen increases

the rate of reaction. Moreover, assuming that the production does not change with the composition of the gas and this is nearly correct, we can explain the effect of foreign gases by variation in the  $N_2^+$  ion production, as derived from a consideration of the ionisation potential of the gases, and the probability of collisions of the second kind.

	$N_2$	$O_2$	Ar	He
Ionisation Potential in Volts	16.8	14.1	15.7	24.5

The ionisation potential of argon lies between that of  $N_2$  and  $O_2$ , hence the possibility exists for an  $Ar^+$  ion to transfer its charge to  $O_2$  by collision of the second kind, i.e.,  $Ar^+ + O_2 = Ar + O_2^+$ . This possibility does not exist with  $N_2$ . Argon, therefore, when added to a nitrogen-oxygen mixture will markedly decrease the ratio of  $N_2^+$  to  $O_2^+$ . The decrease in  $N_2^+$  ion production corresponds to the decrease in the observed rate of synthesis. The absence of any effect of added helium on the rate of reaction is doubtless due to the fact that a transfer of energy by collision of the second kind takes place readily between  $He^+$  ions and nitrogen,  $He^+ + N_2 = He + N_2^+$  (24 volts) forming in this case 24 volts ion. On the other hand, the greater difference in the ionisation potentials of He and  $O_2$ , makes the probability of such a transfer from He to  $O_2$  very small.

Brewer and Westhaver further observed that the synthesis of ozone is due largely if not entirely to positive ions. Since atoms and radiation in the extreme ultra-violet are present in the discharge the possibility exists that both atomic and photochemical mechanism are also in evidence. Fortunately, it was possible for them to get an idea of the relative efficiencies of these various processes. The yield pressure relation indicated that neutral atoms are comparatively inactive in the reaction process. The design of the apparatus was such that a direct test could be made for the amount of ozone produced by radiation and it was concluded that the efficiency of this process is very low, not of the same order of magnitude as that for positive ions.

#### (5) THE THEORY OF CRITICAL ACTIVATION BY KINETIC IONS SUGGESTED BY DONNAN.<sup>49</sup>

The fundamental idea underlying this theory is due to Donnan. He suggested that

<sup>49</sup> Elliot, Joshi and Lunt, *Trans. Farad. Soc.*, 1927, 23, 57-60.



the velocity of chemical reactions might be associated with the number of collisions between ions and gas molecules in which the energy of the ion is equal to or exceeds a certain critical value. Starting on this basis, Elliot, Joshi and Lunt postulate that the concept of "Critical activation" may be applied to chemical action in electrical discharge. They assume, as in the collision theory of chemical activation, that the reaction rate is a function of the kinetic energy of the constituent particles, and that it is immaterial whether the kinetic energy be of thermal or electrical origin. According to this idea the activating energy might be the sum of kinetic energies of thermal and electrical origin. Now Elliot and others obtain an expression relating the velocity of such chemical reactions to the gaseous pressure and to the electrical factors which determine the discharge. In obtaining this expression they assume in order to simplify the discussion, that the radiations arising in the discharge produce no chemical changes.

Consider 1 c.c. of gas, at a pressure  $p$ , which is subjected to the discharge for a small period of time  $T$ . If  $N$  is the number of ion-pairs per c.c. and  $v$  their average velocity in the direction of the field, then  $2vNT$  is the total ionic path traversed while the gas is subjected to the discharge. An ion which travels a distance  $x$  in the direction of the field  $E$  acquires an energy  $eEx$  due to the field, where  $e$  is the ionic charge. If the critical activation energy for the reaction concerned is  $V_0e$ , then  $x_c$  the corresponding critical ionic path is  $V_0E^{-1}$ . According to the classical kinetic theory which is assumed to be valid under the conditions obtained in the discharge,  $c$  the number of collisions of an ion per centimetre of its path which terminate free paths equal to or greater than  $x_c$  is given by

$$c = C \cdot e^{-\frac{x_c}{l}} = C \cdot e^{-\frac{V_0}{El}}$$

where  $C$  is the total number of collisions per centimetre of ion path and  $l$  the mean free path of the ion. Therefore the number of gas molecules changed chemically per c.c. in time  $T$  is

$$2 Nv.T.C \cdot e^{-\frac{V_0}{El}}$$

and  $K$  the velocity of the reaction or the number of molecules changed per second is given by

$$K = 2 Nv.C \cdot e^{-\frac{V_0}{El}}$$

Since  $C$ , the number of collisions per centimetre of the ion-path is proportional to the pressure  $p$ , we can write  $C = k p$  where  $k$  is a constant.

Substituting we get

$$\frac{K}{p} = 2k.Nv \cdot e^{-\frac{V_0}{El}}$$

If  $i$  is the current per sq.cm. carried by the gas then  $i = 2 Nve$  or  $Nv = i/2e$  and the mean free path of the ions  $l = \frac{1}{C} = \frac{1}{kp}$ .

We get making use of these values of  $Nv$  and  $l$

$$\frac{K}{p} = \frac{k}{e} \cdot i \cdot e^{-\frac{eV_0}{EI}}$$

which may be written as,

$$\frac{kV_0}{E} = \frac{1}{p} [\log \frac{k}{e} + \log i - \log \frac{K}{p}]$$

In this form the equation may most readily be tested by experiments carried out with a constant field  $E$ . For then  $kV_0/E$  is constant, which means that the term on the right must also be independent of pressure.

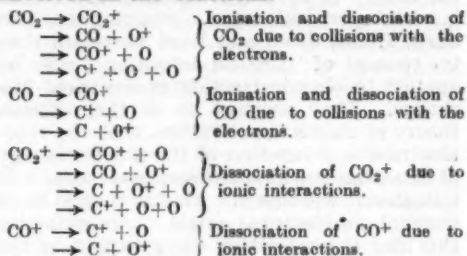
#### CONCLUDING REMARKS.

The fact that chemical reactions accompany the electrical discharge is known for a long time. The well-known examples of such transformations are: the formation of ozone, the synthesis of ammonia, the polymerisation of hydrocarbons, the dissociation of the oxides of carbon or the formation of atomic and chemically active hydrogen. These chemical reactions are in general in no way connected with the mechanism of the discharge. The real function of the discharge is to set going certain fundamental processes. In the ordinary process of electrolysis, the ions not only carry the current, but are also the agents which produce the chemical reaction. In the gaseous discharge the function of the ions is entirely different. As a consequence it is impossible to obtain any law which is the equivalent of Faraday's law of electrolysis. If however in a particular discharge, the ionisation is proportional to the current, then it is likely that the rate of chemical change is also proportional to the current. The constant of proportionality is, not a universal constant like the Faraday constant, but would be different for different processes, and would also change for the same process if the conditions in the discharge tube are altered. In the

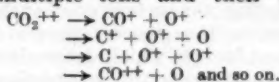
electrical discharge we come across both the formation and the destruction of chemical compounds. Further, the walls of the discharge tube serve as a sort of catalyser, this is specially evident in the conversion of atomic hydrogen to molecular hydrogen. The standard precaution which we must take, if we want to obtain atomic hydrogen in fairly large quantities, is to use fairly long discharge tubes. In short discharge tubes the atomic hydrogen although formed, is very quickly reconverted to molecular hydrogen. A discharge, once it is started soon reaches a condition of equilibrium, so that the number of fresh ions formed is equal to the number of ions lost by neutralisation. Exactly in a similar manner the chemical reaction also reaches a condition of equilibrium. This state of equilibrium is a complex function of a number of variables, and it is not permissible to apply to this state the ordinary principle of thermodynamic equilibrium. Lastly, it is possible to obtain in the discharge tube, chemical combinations which we rarely observe under the every-day conditions. These combinations are the free radicals, the molecules of rare gases or the metallic compounds of rare gases. These combinations are, however, not stable and are destroyed in a fraction of a second.

Up till now it has not been possible to give a single general theory which will explain all the chemical reactions observed in a discharge tube. All that has been done is to perform a number of experiments, in which the rate of synthesis is observed as a function of some known parameter like the current strength, the pressure of the gas or the composition of the gaseous mixture. A number of experiments have also been performed by Brewer and Westhaver to investigate the factors which determine the condition of chemical equilibrium. The experimenters then try to interpret and explain their results on the basis of one of the five theories which we have already discussed. This difficulty of explaining all the reactions in terms of a single theory is due to the fact that in a discharge tube we are not dealing with a single fundamental process like the ionisation or excitation of molecules. But we have a series of reactions which follow one another. I should like to illustrate the complexity of

the process by considering the discharge through carbon dioxide. The following is the list of only the elementary processes involved in the reactions.



In addition to this we come across multiple ions and their dissociations, e.g.,



In addition to this we come across the processes of neutralisation, and the interactions between the different products of reaction. Here we are really dealing with dynamical mixture of charged and neutral molecules and atoms of oxygen, carbon, carbon monoxide, and carbon dioxide, and it is but natural that, in a case like this the discussion of detailed reactions should be accompanied by difficulties.

Now as for the theory of the chemical reactions in the discharge tube, it is possible to get some idea by considering again the five suggestions made in the last section. Thus the 'photochemical theory of Warburg' says that the chemical reaction is due to the excited atoms and molecules, while in the 'static-ion theory of Lind' the union of positive and negative ions results in a chemical change. The 'ion-cluster' hypothesis is of Rice assumes the formation and dissociation of the ion-complex. The 'law of chemical equivalence' of Brewer and Westhaver is only applicable under saturation conditions. While Elliot, Joshi and Lunt assume that the hypothesis of 'critical activation' of Donnan is applicable to the electrical discharge. In the end, we are required to say that these different assumptions are only hypothesis at their best and although they have many useful applications still no single unified theory chemical effects in electrical discharge has been put forward.

## INDUSTRIAL OUTLOOK.

### The Indian Glass Industry.\*

By E. Dixon, A.M.I.Mech.E.,  
Industrial Research Bureau.

#### RAW MATERIALS.

**Chief Raw Materials.**—All Indian glassware is of the soda-lime variety. Lead and potash glasses are not made on account of the high price of red lead, litharge, and potassium carbonate, none of which are strictly indigenous products: although red lead and litharge are made in Calcutta from Burma lead.

For the production of soda-lime glass the chief raw materials required are pure sand (silica), lime and soda ash (sodium carbonate), and also fireclay and fuel. All of these, with the exception of soda ash, are found in abundance in India, but unfortunately there is no place in the country where they are all found together in large quantities so that no particular district can be said to be favoured as a glass-manufacturing centre above all others.

In addition to the main raw materials enumerated above small quantities of special materials are required as oxidising, reducing, colouring, decolouring, and opacifying agents. These will be described in more detail later, but it may be mentioned here that nearly all of them have to be imported.

The process of manufacture consists of fusing together in suitable furnaces the sand, lime and soda ash and such small quantities of the special materials as are necessary for the particular type of glass being made. The sand (silica) which is acidic is decomposed at a much lower temperature in the presence of the sodium carbonate and lime than it would be in their absence. In general terms it may, however, be stated that the lower the alkali content the more durable the glass. The most resistant of all glass, e.g., 'Pyrex', is practically pure fused silica and boric oxide, and the alkali content is only about 5 per cent.

**Sand.**—From the glass-maker's point of view the most objectionable impurity commonly found in sand is iron oxide; very small quantities of this material are sufficient to tint the glass green or straw

coloured, and to spoil the much desired brilliancy. For the manufacture of the finest colourless glassware very pure sand containing not less than 99% silica and not more than 0.02% iron oxide is desirable. In addition, not less than 95% of the sand should pass a 30 mesh per inch sieve and be retained on a 100 mesh per inch sieve, as it is important that the sand should have a uniform grain size and not contain a large proportion of 'fines'. (Very fine sand is liable to be carried by gas bubbles to the surface of the glass where it forms 'stones' by reason of its comparative immunity there from the fluxing action of the alkalis.)

It is doubtful whether India possesses glass sand of this quality, but there are many deposits suitable for the manufacture of good decolourised glass, i.e., sand in which the iron oxide content does not exceed 0.10% so that the green tint imparted to the glass is sufficiently pale to permit of decolourising by superimposing a pink tinge from small quantities of such materials as manganese dioxide or selenium. If the iron oxide content of the sand exceeds 0.10%, decolourising cannot successfully be carried out as the glass takes on a greyish hue and lacks brilliancy.

Much of the sand used by the industry is obtained from deposits of friable sandstone at Bargarh and Loghara near Naini in the United Provinces. A deposit with a good reputation is situated at Sawai Madhopur near Jaipur and is used by many of the Firozabad bangle-makers. There are also suitable deposits at Jaijon in the Hoshiarpur District, Jubbulpore and Madras. Glass sand can usually be improved by washing and screening but few Indian glass manufacturers do more to purify their sand than give it an elementary screening.

**Lime.**—Limestone is found in abundance in India and the glass industry suffers from no lack of excellent and cheap supplies of this material, either in its natural form or burnt to quicklime. Since most of the furnaces are pot furnaces, where

\* Continued from page 130.

the glass is melted in closed fireclay pots, quicklime or slaked lime (quicklime quenched with water) is usually used. Limestone, which has a less vigorous action than either quicklime or slaked lime, is used chiefly in tank furnaces where the glass is melted in contact with the flames and combustion products of the furnace and, therefore, usually reaches higher temperatures than when melted in glass pots. Pure quicklime contains 100% calcium oxide, pure slaked lime 75.7% and limestone 56%. As in the case of sand the most objectionable impurity is iron and this should not exceed 0.15% for good quality glassware, but for decolourised ware up to 0.30% iron is permissible. Many of the factories use lime from the enormous deposits at Katni, near Jubbulpore, in the Central Provinces.

**Soda ash.**—The third essential bulk raw material required for the manufacture of soda-lime glass, soda ash, is not produced in India in commercial quantities, and practically the whole of the supplies for the industry are imported. Small quantities of natural sodium carbonate are obtained from time to time from Lona Lake in the Central Provinces, but they are negligible compared with the demands of the glass industry.

Attempts have been made to manufacture soda ash in the country, notably at the Shri Shakti Alkali Works, Dhrangadra State, in Kathiawar and, during the War, by extracting sodium carbonate from *reh* deposits, but they have met with limited success. It is, however, understood that plans for the manufacture of soda ash on a large scale from the waste salt of the Khewra mines are nearing completion, so that it is probable that India will eventually have ample indigenous supplies of this material.

**Fireclay.**—India is fortunate in possessing large deposits of excellent fireclay admirably suited to the manufacture of glass. Most of the requirements of the industry are met by Messrs. Burn & Co., Jubbulpore, and Messrs. Bird & Co., Kumardhubi, but there are other suppliers, including Messrs. Burn & Co., Raniganj (silica and sillimanite) and Messrs. The Perfect Potteries, Jubbulpore. For use in the glass industry, fireclay is made into firebricks and blocks for the construction of the furnaces and annealing ovens. It is

also shaped into glass pots or crucibles, for the pot furnaces, although at present most glass pots used in the industry are imported from Japan.

An essential requirement for fireclay refractories which are in contact with molten glass is that they must be chemically neutral—neither acidic nor basic—or they will rapidly be attacked by the glass. Silica, and lime or magnesia refractories are equally unsuitable for the purpose. In addition the refractories must be dense, mechanically strong and capable of resisting for long periods temperatures as high as 1,500° C. They should also have a very low coefficient of thermal expansion or contraction.

To comply with these exacting conditions the fireclay used, must contain such fluxing materials as lime, magnesia, potash and soda, in very small quantities only. It is not possible to dispense entirely with all of these 'impurities' as they are largely responsible for the plasticity of the clay. The clay should also be free from iron in appreciable quantities as, in the case of tank blocks, this will tend to dissolve into the glass. An analysis† of a typical Jubbulpore clay given below shows that chemically, and as far as resistance to high temperature is concerned, these conditions are admirably met, and the clay there analysed compares well with similar English fireclays. Good as these refractories are, however, they will not withstand the corrosion at the glass level of high temperature tank furnaces for long, and for prolonged service super refractories must be employed in such places.

**Sillimanite.**—Much research work has been done during recent years on the subject of glass refractories and it is nowadays generally conceded that the substance which most satisfactorily fulfils the exacting requirements of glass tank service is

† Analysis of Jubbulpore Fireclay:

		%
Silica	..	68.25
Alumina	..	27.95
Iron oxide	..	1.10
Titanium oxide	..	1.66
Lime	..	0.50
Magnesia	..	0.20
Loss on ignition	..	0.20
		<hr/> 99.86

Fusion Test, Seger Cone 31/32 (1690° C./1710° C.).



the compound aluminium silicate corresponding to the formula  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , in the crystalline form known as sillimanite. This mineral, which is tough and strong, has a melting point of over  $1800^\circ\text{C}$ . and does not soften appreciably below this temperature; it has a very small coefficient of thermal expansion; it has great chemical stability and is neutral in composition.\*

Another substance with the same chemical composition is kyanite, but this is not so satisfactory as a refractory as the coefficient of thermal expansion is much greater than in the case of sillimanite. Moreover, the hardness of kyanite is not the same along different planes. Kyanite can, however, by calcination at  $1450^\circ\text{C}$ ., be converted to a substance known as 'mullite' which is very similar to sillimanite.

Massive sillimanite is very scarce throughout the world, and India is fortunate in possessing some of the few deposits of this super refractory so far discovered. Deposits of kyanite also exist in this country. The deposits of kyanite are described in the *Memoirs of the Geological Survey of India*, Vol. LII, Part II, and exist at Sona Pahar, Nongstoin State, Assam, near Shillong; at Pipra in Rewa State, Central India, about 100 miles from Mirzapore, and in the Banda District of the Central Provinces. There are deposits of kyanite at Singhbhum. Unfortunately, the sillimanite deposits are very inaccessible and the material is costly to mine. Moreover, it is extremely hard and the crushing costs are high, so that at present it is little used by Indian glass manufacturers: but small quantities of sillimanite refractories are made for the industry by Messrs. Burn & Co., Raniganj. Most of the sillimanite and kyanite mined is at present being exported raw, chiefly to America.

**Fuel.**—With the exception of a few

charcoal and wood fired bangle furnaces, and the spangle glass furnaces at Panipat, all Indian glass furnaces are coal fired. Usually the coal is not gasified before burning but is 'direct fired' on the grates of the so-called 'Japanese' furnaces which are to be found in the great majority of the factories. As previously mentioned these furnaces are inefficient and for their successful operation they require good quality, long flame coal: the better qualities of coal from Jharia and Raniganj are, therefore, universally used. The price of coal at the factories varies enormously with their distance from the coal fields, but in all cases fuel is the most expensive of the cost items for the main raw materials, and the reduction of fuel charges by the introduction of better furnaces is one of the most obvious needs of the industry.

During the survey of the industry carried out by the Industrial Research Bureau in 1935-36 the average ratio of fuel burned in the furnaces to the batch materials melted was found to be 1.6 to 1. In modern glass furnaces a ratio of 0.8 to 1 is not uncommon.

**Special Raw Materials: Borax.**—This is frequently used in Indian glass batches, the acid boric oxide, replacing some of the silica. It is obtained from Tibet and used in comparatively small quantities.

**Oxidising Agents.**—In India the chief oxidising agent employed in glass manufacture is saltpetre. It is used in glass batches containing easily reducible substances which it is desired to keep in their oxidised form. The colouring effect of iron can be minimised by oxidising the iron to the less highly coloured ferric state. Saltpetre is added in small quantities to almost all Indian glass batches and is a common product of the country.

**Reducing Agents.**—The reducing agent commonly employed in the industry is carbon in the form of finely crushed coal. Reducing agents are added to glass batches containing materials which it is desirable to reduce in oxygen content. For instance, sometimes sodium sulphate (salt cake) is added as a partial substitute for soda ash to batches melted in the few tank furnaces which exist in India. When this is done a reducing agent is also added to reduce the sodium sulphate to sodium sulphite which is a more active fluxing

\* Chemical Analysis of Sillimanite :

		%
Loss on ignition	..	0.80
Silica ..	..	33.90
Titanium ..	..	1.72
Iron oxide ..	..	1.80
Alumina ..	..	61.18
Lime ..	..	0.51
Magnesia ..	..	Trace
Alkalies ..	..	Nil
		99.90

material. Reducing agents are employed in the production of colours from metallic oxides when the colouring agent must be present in a metallic state.

**Colouring Agents.**—The colouring of glass is accomplished by introducing certain metallic oxides and elements. The following is a list of colours commonly obtained in India, together with the colouring agents used. The colouring effect of these materials is usually very strong, and small quantities only are required to produce the desired effect. On the other hand, nearly all the materials have to be imported and are expensive.

COLOUR	COLOURING AGENT
Red ..	.. Selenium with or without cadmium sulphide
Yellow (Gold) ..	.. Cadmium sulphide
Yellow with a greenish Fluorescence	.. Uranium oxide
Aquamarine blue ..	.. Copper oxide or copper sulphate
Blue ..	.. Cobalt oxide
Green (Lemon) ..	.. Potassium dichromate and copper oxide
Green ..	.. Iron oxide
Violet ..	.. Manganese dioxide
Amber ..	.. Carbon (coal)
Yellow Amber ..	.. Sulphur

The production of good colours is a matter requiring considerable skill and experience and often depends upon the condition of the atmosphere inside the pot or tank. For instance, the colours produced by iron and manganese vary widely with the degree of oxidation. Some of the colouring agents such as manganese, nickel, chromium and iron form coloured silicates, others, such as selenium and carbon enter the glass in a colloidal form. The Firozabad bangle glass-makers are adepts at producing varied and beautiful colours, but nearly all of the ordinary blownware factories produce small quantities of simple coloured ware such as tumblers, vases, lamp-shades, globes, etc.

An iridescent effect is obtained by some glass-makers by spraying the article, whilst still hot, with ferric chloride, and the Firozabad bangle-makers frequently give a glistening silver appearance to their bangles by spraying them with silver nitrate.

**Decolourising Agents.**—The decolourising of Indian glass is accomplished by adding to the batch manganese dioxide (a product of India) or selenium (an imported element usually associated with sulphur). Both of

these materials produce a pink colour when added in small quantities, and this serves to cover the familiar iron green tinge.

**Opacifying Agents.**—Indian batches for opal glass always contain fluorspar (calcium fluoride) and cryolite (sodium aluminium fluoride). The opal effect is caused by the fine colloidal dispersion which occurs in the glass when these materials are used. Both of these materials are imported.

**Alkaline Rocks.**—There are in India several large deposits of alkali containing rocks and minerals which are very suitable for the manufacture of glass. The chief of these are feldspar, both albite (soda) and orthoclase (potash), and nepheline syenite. Analysis of these materials yields approximately 55/56% silica, 19/22% alumina and about 15% total alkalis, besides small quantities of iron, calcium, etc. It will readily be seen that their chief use is as a means of introducing cheap alkalis into the batch and so reducing the amount of costly soda ash required.

The chief difficulty experienced in using these materials on an economic scale is due to the large amount of alumina they contain, as alumina, when present in the glass batch in quantities exceeding 2 or 3 per cent., greatly increases the viscosity and so the founding temperature. In consequence, with the exception of a little feldspar (for some reason unknown this is usually imported) which is generally added to opal batches to assist in promoting the opal effect, these materials are not at present used in the Indian glass industry, as the existing furnaces cannot maintain sufficiently high temperatures to found highly aluminous glasses.

The subject has been studied by Dr. V. S. Dubey and P. N. Agrawalla of the Benares Hindu University\* who reached the conclusion that nepheline syenite is the most suitable indigenous rock for the partial substitute for soda ash in the Indian glass industry. (The ratio of alkalis to silica is higher in the case of nepheline syenite than in the case of feldspar.) They suggested that it might be freed from iron by magnetic separation and used in glass batches in quantities equal to the silica content.

\* Bulletin No. 7 of Indian Industrial Research. "The Utilisation of Nepheline Syenite Rock as a Partial Substitute for Soda ash in the Glass Industry of India."

The chief deposits of felspar are at Ajmer, Kishengarh State, Rajputana, Bihar, Eastern Bengal and Madras. It is often found with mica. Nepheline syenite is available in large quantities in Kishengarh, and to a lesser extent in Kathiawar and Madras.

One of the methods of assisting the industry decided on after the survey by the Industrial Research Bureau was the publishing of a complete survey of the raw materials available in India. The geological work is being carried out by Dr. V. S. Dubey of the Benares Hindu University and the samples are being tested and classified at the Government Test House, Alipore, Calcutta.

ARTICLES MANUFACTURED—VALUE OF THE  
INDUSTRY—MANUFACTURING PROCESS AND  
EQUIPMENT—COMPOSITION OF INDIAN  
GLASS.

*Articles Manufactured.*—About 60% of the production of nearly all Indian glass works consists of oil lamp globes and chimneys. Next in numbers manufactured are blown stoppered glass bottles or jars used for the storage of food-stuffs. Hand-blown medical and other bottles are also made in large quantities. Cheap blown tumblers and a few pressed tumblers form an important line of production, but very little fancy or high class glassware is made.

A few works produce cheap laboratory ware such as beakers, phials, test-tubes and hand drawn glass tubing. Only one factory, the United Provinces Glass Works, Bahjoi, U.P., manufactures sheet-glass, the Fourcault drawing process being used. Generally speaking, the quality of Indian glassware is somewhat inferior to that of similar imported ware.

*Value of the Industry.*—In 1935-36 it was estimated that blownware and sheet-glass to the value of about Rs. 37 lakhs, and bangles to the value of Rs. 30 lakhs approximately were annually being produced in India. These estimates are probably conservative. The total value of imports of glassware in 1936-37 was Rs. 128 lakhs approximately.

*Manufacturing Processes.*—Nearly all Indian glassware is hand-blown. Very little pressed ware is made, and although three factories, the Allahabad Glass Works, Naini, United Provinces, the Bombay

Glass Works, and the Calcutta Glass and Silicate Works, possess bottle blowing machinery, these are not at present in use. As previously mentioned most manufacturers melt their glass in direct fired pot furnaces, known colloquially as 'Japanese' furnaces.

*Tank and Pot Furnaces.*—There are two main types of glass furnaces, the tank furnace and the pot furnace. In the tank furnace the batch materials are melted in a large covered fireclay chamber, or tank, which forms part of the furnace itself. Gas (and sometimes oil) is introduced with a suitable supply of preheated air through the tank walls above the batch, and combustion takes place in contact with the glass. This type of furnace is suitable for the continuous production of large quantities of glass, raw materials being fed in at one end of the tank and glass withdrawn at the other. There are very few tank furnaces in India, where the average factory produces only two or three tons of glass daily.

The other type of furnace produces glass in fireclay pots or crucibles, the pots being enclosed in a fireclay pot chamber, or dome, into which the flames and products of combustion from the furnace proper are led. This type of furnace is intermittent in action and is capable of producing finer glass than the tank furnace, as when closed pots are used, the glass does not come into contact with the products of combustion.

*The 'Japanese' Furnace.*—The so-called 'Japanese' furnace universally used in India is a furnace of the second type. The coal is burned on an open grate below the pot chamber into which the flames and hot gases rise through a hole (the 'eye') in the centre of the chamber floor. The pots stand in a circle round the eye and the products of combustion pass away to the chimney through small flues in the walls of the pot chamber. In order that the flames may be caused to envelope the pots, the furnaces are operated with the maximum of draught. This results in enormous quantities of air in excess of the combustion requirements of the fuel being drawn through the furnace, which consequently can never attain really high temperatures. It also results in very high fuel consumption.

Modern glass furnaces, whether tank or pot furnaces, are all fitted with devices for utilising waste heat. These devices not only make for economy of fuel consumption but also ensure higher temperatures than are possible in direct fired furnaces. The coal is not burned completely in one operation, but it is first gasified in a 'producer' by burning it with a limited air supply, or with an injected mixture of steam and air, so that carbon monoxide and hydrogen are formed instead of carbon dioxide and water vapour. The gas is led to the furnace and combustion is completed in a convenient position (e.g., over the batch mixture in a tank furnace, or in the 'eye' of a pot furnace) by means of a controlled supply of air pre-heated by the waste gases.

*Regenerators and Recuperators.*—There are two well-known air pre-heating devices, the regenerator and the recuperator. In regenerative systems the hot waste gases from the furnace are controlled by a two-way valve and are caused to pass alternately through two sets of two chambers each filled with chequer brick work, before passing on to the chimney. When one set of these chambers has become sufficiently heated the valve is reversed and the waste gases are thereby caused to flow through the other two chambers, which previously had been passing the gas and air to the furnace. Simultaneously, the gas and air are now caused to pass through the pre-heated chambers before entering the furnace. When the original gas and air chambers are sufficiently heated the valve is again reversed, and the operation is repeated at about half hourly intervals throughout the working of the furnace. It will be seen that the method is intermittent and that flames are generated inside the furnace on alternate sides, as the flue openings, which are placed opposite to each other in the furnace, become alternately burners and waste gas outlets.

The other pre-heating device, the recuperator, consists essentially of a series of fireclay tubes which carry the waste gases from the furnace to the chimney flue. The incoming 'secondary' air is caused to flow round these tubes and so attains a considerable degree of preheat before entering the furnace. Opinions vary regarding the respective merits and demerits of the two systems, as in the case of the regenerator

the heat is applied alternately from side to side of the furnace, while in the case of the recuperator there is danger of leakage in the recuperator tubes, although the combustion flames and products are always propagated in one direction. Actually, both systems are thoroughly tried and proved and one or other of them is essential to any modern furnace.

Usually, the regenerator is applied to the large glass tank furnaces as in such furnaces the alternating heating effect is not so pronounced on account of the great quantities of heat stored in the furnace walls and in the glass. The few tank furnaces which exist in India are made on this principle. The recuperator is ideal for small pot furnaces and it is astonishing to find no furnace fitted with this device in India.

The Industrial Research Bureau has designed a recuperative pot furnace of the size commonly found in India—9,800 lbs. pots—and the furnace will shortly be erected in Firozabad, United Provinces, where it is hoped to demonstrate its advantages.

*Method of Manufacture.*—The methods of manufacture practised by all Indian glass manufacturers in the production of hand-blown ware are substantially the same, so that a brief description of the manufacture of lamp globes, the chief line of production, will cover the manufacture of other blown articles in all except minor details.

The batch materials are weighed out, hand mixed and placed in the glass pots in the evening along with quantities of cullet (broken waste glass from the day's blowing). The fire is banked up and melting proceeds during the night. After melting is complete the glass is 'fined' for about an hour before using. During the fining period the temperature of the furnace is lowered slightly and the glass freed from bubbles as far as possible. To assist this process vegetable matter, such as potatoes, is sometimes thrown into the pots, but it is more usual to include in the batch small quantities of a volatile material such as arsenious oxide in order to liberate the 'seed' bubbles. After fining is complete the covers of the pots are removed and the glass allowed to cool to about 1,000° C. at which temperature it has a suitable viscosity for working.



When the glass is ready for "working out" a long iron blow pipe is inserted into the pot by the blower's mate and a portion of glass collected at the end. By blowing and swinging, this is formed into a small bulb. The pipe and bulb are then transferred to the blower who stands over a cast iron mould mounted in a small pit in the ground. The mould, which is in charge of a mould bay, is split down the middle and hinged so that it can be opened for the insertion of the bulb of glass. After closing the mould the glass is inflated by blowing to the shape of the interior of the mould. Sometimes moulds are lubricated during this process by the insertion of a sheet of paper along with the glass, carbon formed during the combustion of the paper acting as a lubricant.

After blowing the globes (globes are usually blown in connected 'strings' of two or more) are cracked off from the pipe and sent to the annealing lehr.

**Annealing.**—During the process of manufacture glass articles become strained and it is necessary to remove these strains by annealing, otherwise the glass will readily break in service. In India annealing is done by stacking the glass-ware in simple annealing kilns or lehrs, which are heated by small open fires built inside the kilns in one corner. The kilns are merely brick chambers about 10 × 6 × 6 feet with a filling door in the front wall and a chimney connected to the rear wall. The fire is tended through a special opening in one corner of the front wall.

When the kiln is full the filling door is closed and the temperature raised to about 500° C. The door is then opened and the fire drawn and the kiln allowed to cool down to room temperature, when the articles are removed for finishing and packing. This process of annealing is slow and there is a great deal of breakage during the filling and unloading of the kilns.

Modern glass works use continuous, gas heated lehrs which reduce breakage to a minimum. The glassware is loaded on an endless metal belt which runs through a gas-heated tunnel. The heating is under exact control and the temperature of annealing can be adjusted to the particular kind of glass passing through the lehr. After travelling through the heated portion of the tunnel the glass is subjected to controlled

cooling as it proceeds on its journey to the discharge end of the lehr, and it is finally discharged cool enough to be handled.

Lehrs of this or similar types will eventually have to be used here if India is to hold her own as a glass producing country.

**The Composition of Indian Glass.**—The composition of glass is conventionally expressed in terms of the constituent oxides. The main constituents of a typical Indian blownware glass expressed in these terms and based on an average of seventeen batches are given below:

	% .. .. ..			
Silica	..	..	..	74
Sodium oxide	..	..	..	17.4
Calcium oxide	..	..	..	6.8
Potassium oxide (from saltpetre)	..	..	..	1.4

A glass of this composition will be easy to melt but, on account of the high percentage of sodium oxide, will have a high coefficient of thermal expansion and, therefore, will be liable to crack when subjected to sudden temperature changes. Moreover, the glass will be slightly water-soluble even in cold water, and so will quickly lose its brilliance when exposed to the atmosphere. These characteristics are amplified by the potassium oxide present, as this material gives to glass similar properties as sodium oxide, although in a somewhat lesser degree.

Such a glass is quite unsuitable for the manufacture of medicine bottles, although in India similar glasses are sometimes so used.

The glass should contain more calcium oxide and less sodium and potassium oxides, as calcium greatly increases the hardness and decreases the solubility, although it increases the tendency towards devitrification and also increases the founding temperature somewhat. A glass containing about 12% of sodium and potassium oxides and about 12% of calcium oxide would be harder, cheaper and more durable, and could easily be melted in recuperative or regenerative furnaces, but such a glass could only be melted with the greatest difficulty in the existing direct fired pot furnaces. It appears that the development of the Indian glass industry is largely bound up with the improving of the furnaces and lehrs.

**College of Agriculture and Agricultural Research Institute, Coimbatore.**

By R. C. Broadfoot.

*(Agricultural College, Coimbatore.)*

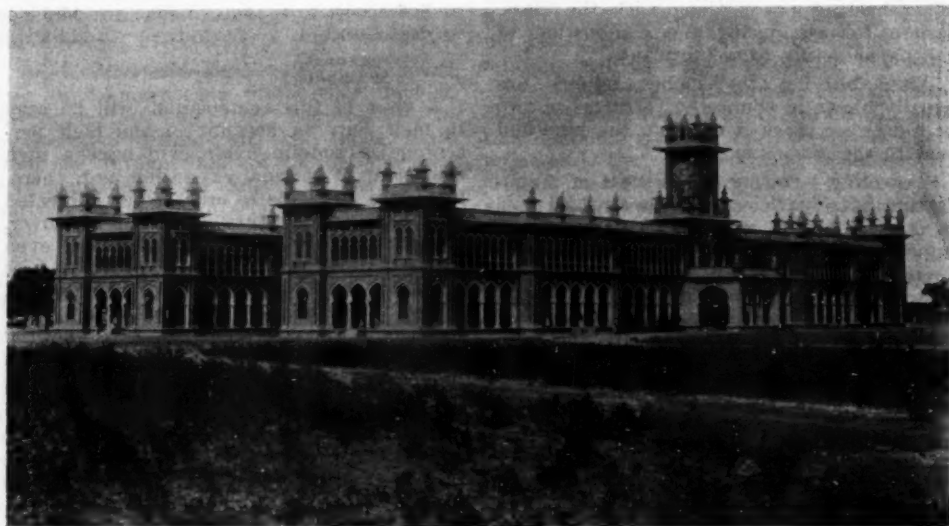
**T**HE Institute owns a Library with 39,000 volumes. About 600 scientific periodicals are regularly received. The Madras Herbarium which contains 83,240 mounted sheets is housed in the Research Institute.

**COTTON SECTION.**

This section was added in 1920, as a result of the recommendations made by the MacKenna's Indian Cotton Committee of 1919.

assist and advise the Deputy Directors of Agriculture with regard to cotton work carried out in their circles.

As a result of breeding work conducted at the Cotton Breeding Station, a strain—Co-2—which gives a yield of 15 per cent. more than the unselected bulk was isolated in 1928. This strain has now spread over an area of more than 1.6 lakhs of acres in the Presidency. Recently, two more strains have been evolved and they bid



Agricultural Research Institute, Coimbatore.

At present, it has a staff of a Cotton Specialist, 8 Assistants at the Headquarters, 2 Assistants at each of the Agricultural Research Stations of Koilpatti, Hagari, Nandyal and Guntur. A farm of 86 acres comprising of red and black soil areas is attached to the section at Coimbatore for the conduct of several experiments connected with cotton crop. The main object with which this section was opened is to improve the growing of Cambodia cotton by means of breeding and agronomic methods, to train persons to take up similar work in other cotton areas of the Presidency and to

fair to be more popular. Attempts are on foot to effect further improvements in earliness, productivity and spinning quality. One of the latest strains has already shown to be a month earlier than Co-2 with no drop in other characters. On the agronomic side sowing Cambodia in September and irrigating it once in three weeks have been found to be beneficial.

In addition to these, four schemes financed by the Indian Central Cotton Committee are being run under the Cotton Specialist with objects of either producing strains suited to special regions or devising

measures to get rid of the defects found in the existing agricultural practices relating to cotton cultivation.

Recently, breeding work in the Bengal and red grams was also started with a view to reduce, if not to stop completely, large quantities of pulses (worth about Rs. 150 lakhs) that are being imported into this Presidency. In the former crop, two strains yielding more than 15 per cent. over the locals and resisting wilt, have already been evolved.

#### PADDY SECTION.

The Government Economic Botanist Section was split in 1912 into Government Economic Botany and Government Lecturing Botany Sections to deal with breeding in crops and teaching respectively. The first Economic Botanist Mr. F. R. Parnell took up the duties of the Government Economic Botanist in 1913 and commenced work on rice and cotton. With the rapid development of work on rice which required all his attention, very little attention was paid to cotton. With the retirement of Mr. F. R. Parnell in 1923, the post was designated as Paddy Specialist.

The main problems that have been undertaken for study in this section are:—

(i) Making a collection of paddy varieties, isolating and maintaining pure lines from them. The present collection, Indian and Foreign together, number over 1,300.

(ii) Study of characters (both morphological and economic) of the rice plant and understanding their mode of inheritance. The results of the study have been written up in the form of *Memoirs of the Pusa Institute* (Botanical Series).

(iii) Evolution of more prolific strains by simple selection from the important local varieties of the main rice tract of the Presidency at the main station Coimbatore and its sub-stations at Aduturai (1921), Marutur (1925), Pattambi (1926) and Berhampore (1932). So far 44 strains yielding from 10-15 per cent. over the respective local varieties suitable for the *Kar* (short duration) and *Samba* (long duration) seasons are now under cultivation in the paddy areas of the Presidency, not to mention of about dozen strains on the threshold of being distributed. It is estimated that about 12,75,000 acres are now cropped with improved strains. This alone is contributing to the increase of wealth of the country by about 50 lakhs of rupees.

(iv) Evolution of strains by artificially hybridising chosen pure lines so that desirable qualities to be found in such pure lines could be synthesised in one strain and also isolation of economic mutants from seeds treated with X-ray. A few strains resistant to Blast disease (*Pyricularia oryzae*) and non-lodging characters are shortly to be released for general cultivation.

(v) A number of agronomic studies of local interest are being carried out in the several sub-stations.

(vi) Work on quality in rice has been taken up and histological study of the rice grain has given much interesting information on the nature and location of proteins in rice grain and the thickness of aleurone layer in different kinds of rices cultivated under different conditions.

(vii) A beginning has been made in the study of the cytology along with the genetics of the rice plant. These aspects of the study will be taken up soon after the return of the Assistant, now under training in England.

#### MILLETS SECTION.

This section of the Agricultural Research Institute was constituted in December 1921. Lands for the Millets Breeding Station were acquired in October 1923. The Station was laid out and work on breeding millets began from the agricultural year 1924-25. There are eight millets and they are in the following order of importance:—

Sorghum	.. ( <i>Sorghum vulgare</i> , Pers.)
Cumbu	.. ( <i>Pennisetum typhoides</i> , Stapf. and Hubbard)
Ragi	.. ( <i>Eleusine coracana</i> , Gaertn.)
Tenai	.. ( <i>Setaria italica</i> , Beauv.)
Kodo	.. ( <i>Paspalum scrobiculatum</i> , Linn.)
and the	( <i>Panicum miliare</i> , Lam.)
panicum	( <i>Panicum miliaceum</i> Linn.)
millet	and ( <i>Panicum crusgalli</i> var. <i>frumentaceum</i> , Linn.)

The improvement of these millets by selection and hybridisation is the work of the section. The botany, genetics and cytology of the millets are under intensive study. Over 90 publications on this fundamental knowledge have appeared in many scientific journals. Millets are so very local in their evolution and spread, that much of the economic work has to be done in the respective local areas. Assistants trained in millets breeding are working in the Bellary, Nandyal, Guntur and Koilpatti areas on the improvement of the local

millets. Ragi, E.C. 593, is however an exceptional instance of a millet that is cosmopolitan enough to get a good name for itself from many parts of the Presidency. Strains of sorghum, cumbu and tenai are in various stages of trial in all the centres mentioned above.

#### OIL SEEDS SECTION.

In view of the importance of the oil yielding crops to the prosperity of the Madras Presidency, a section on oil seeds was organised in 1930 to conduct plant and agronomic research on major oil seeds, viz., groundnut, sesamum, castor and coconut. The field work is carried out on five Agricultural Research Stations attached to the section and located in various parts of the Presidency. Dr. J. S. Patel, Oil Seeds Specialist, is in charge of the section.

**Groundnut.**—In 1934 a mass-selected, superior spreading variety of groundnut was released for cultivation. It gives an average increased yield of 20 per cent. over the local. This variety which is "bold" and reported to be drought resistant, is rapidly replacing the local varieties. One of the high yielding bunch selections is now in the final year of its trial, and it will be distributed for field trial next season. Numerous inter-varietal and inter-specific crosses between *A. Hypogaea*, *A. rasteiro* and *A. Nambyquarae* have been made. The mode of inheritance of the plant characters, viz., habit, duration, testa-colour, chlorophyll deficiency and the colour in the plant and the flower, has been worked out.

The optimum spacing depends upon the rainfall. For South Arcot District,  $9' \times 9'$  spacing for spreading varieties and  $6' \times 6'$  spacing for the bunch, was found most economical. For the same soil, application of ten cart-loads of manure per acre proved remunerative.

The quality and the quantity of oil in the seed was found to depend upon the maturity of the crop and the conditions of storage. The crop should be harvested only at full maturity and the produce should be stored after full drying in well-ventilated dry godowns.

Anatomical and cytological studies and investigations into the vitality and the resting period of the seed have been carried out.

**Coconut.**—Inter-cultivation is found to increase the yield of the garden. Ammonium sulphate and ash, and cattle manure were found to be the most remunerative manures for the West Coast. The conditions under which surface planting of the seedlings is to be recommended were determined. On the West Coast, it is considered uneconomical to grow a subsidiary crop under the breeding coconuts. A green manure crop of cowgram is, however, recommended.

Selection of medium sized round seed nuts from heavy yielding palms, possessing a large number of leaves, is recommended. The seedlings should be further selected in the nursery on the basis of the girth at the collar. First generation of selfed and crossed progeny have been planted with a view to evolve suitable types.

With the aid of anatomical and cytological studies, it has become possible to understand the mode of response of the palm to climatic and edaphic conditions. Such aspects as the abortion of spadices, pollination, germination, root and leaf developments, catalase activity of the leaf, shedding of female flowers and young nuts, development of the nut, tapping in relation to yield have been investigated into.

**Sesamum.**—Types 46 and 89 have proved superior to the local variety. A spacing of  $12' \times 12'$  was found most economical for the irrigated crop. Floral biology and the inheritance of characters have been studied.

**Castor.**—Inbred pure lines having short duration and good yield, have been evolved. Showy horticulture types have also been isolated.

#### MYCOLOGY SECTION.

**History.**—The Mycological Section of the Madras Agricultural Department developed to its present magnitude from very small beginnings. The foundation of this work was laid when the Government Botanist with a single mycological assistant began the investigation of the main diseases of a few crops like sugarcane, pepper and sorghum. Since 1910 when a Mycologist was appointed, the section has made rapid progress with a number of successful investigations to its credit.

The activities of the Mycological Section may be briefly summarised as follows :—



(1) *Economic Research.*—This comprises investigations, both in the laboratory and in the field, into the occurrence, cause, nature, effects and control measures of plant diseases caused by fungi and viruses. Research of this nature involves close observation of the growth, spread and effect of the disease and artificial cultivation of the fungi on suitable media, study of their cultural characters and spore forms which enables them to be identified, inoculation of healthy plants with the pure cultures and various other studies involving special technique. Once an exhaustive study of the life-history and host range of a fungus is made, remedial measures are tried in the light of the knowledge thus acquired, firstly on a small scale within the laboratory or in the pot culture house attached to it and then in the field.

(2) *Advisory Work and Propaganda.*—Advice is given to cultivators all over the province regarding their phytopathological problems. The fruits of research are brought home to the cultivators in the form of leaflets, and by practical demonstrations, lantern lectures, exhibitions, etc.

(3) *Systematic Work.*—The systematic study of fungi is not neglected. Specimens of diseased plants are collected as often as opportunities occur. These are classified and preserved while those of special interest are forwarded to Specialists for identification. A fairly representative herbarium has been built up in Coimbatore and preserved specimens and pure cultures are available for students and to a limited extent for exchange with other countries.

#### GOVERNMENT AGRICULTURAL CHEMIST'S SECTION.

This section has two main functions: (i) *Advisory*, in matters connected with the chemistry of soil, plant and other agricultural products and (ii) *Research*, on problems connected with agriculture and agricultural products.

The staff of the section consists of the Government Agricultural Chemist, four Assistant Agricultural Chemists and one Agricultural Bacteriologist; one of the Assistant Agricultural Chemists is working at Siruguppa (Bellary District) at the Irrigation Research Station, which has been just opened. Each of the officers is in charge of one of the six branches of work,

which are as follows: (i) Analytical and Advisory, (ii) Soil Surveys, (iii) Bacteriology, (iv) Animal and Plant Nutrition, (v) Sugarcane products, and (vi) Irrigation Research. Under the Advisory branch a large number of samples of various kinds are received from ryots, and private parties as well as from planters and advice rendered, based on analysis of the samples. Under the Research branch a number of problems are under investigation in all the branches. The most outstanding pieces of research so far carried out are, the effect of manuring on crop quality, the soil survey of the Tungabhadra Project area, the activation of paddy husk carbon for clarification of cane juice and the studies on the protein and mineral metabolism of cattle; work on many other problems in Agricultural Chemistry is in progress.

#### ENTOMOLOGICAL SECTION.

This section is in charge of Mr. M. C. Cherian, B.A., B.Sc., D.I.C., Government Entomologist, who is assisted in his work by an Assistant Entomologist and six assistants. The main work of the section is economic and is concentrated on the study of the bionomics of, and control methods against, the major insect pests of important crops grown all over the Madras Presidency. The study of live insects is carried on at the Insectary building situated inside the College Estate where facilities are provided for the rearing of and observation of insects and for the trial of various methods of pest control. There is a large and representative reference collection of insects attached to the laboratory where there are facilities for systematic studies. There is also a well-equipped apiary at the Insectary intended for research and propaganda work on the Indian honey bees and practical training is given to those who desire to learn.

It is not possible in a short note of this kind to give even a bare outline of the progress made by the section. The numerous publications including two books *Some South Indian Insects* (out of print) and *Handbook of Economic Entomology for South India* (in press) contain the results of the research work carried out from time to time by different members of the Section. The more important items of work on which research is done at present are sugarcane moth borers and mealy bugs and their natural enemies;

fruit flies and their parasites; the rhinoceros beetle; the cotton bollworms; pests of paddy; stored product pests; pests of vegetables; and the Indian honey bee and its enemies.

#### RESEARCH ENGINEERING SECTION.

This section was established in August 1928 for the purpose of investigating the possibilities of improving the ryots' mechanical farm equipment. A large variety of implements and machines are tested with a view to the determination of the types and makes best suited to Indian conditions and those which are approved are recommended and demonstrated by the Department.

In addition, the improvement of the efficiency of indigenous implements and machines and the evolution of new designs are subjects receiving close attention.

Achievements of the Section are: Testing a wide variety of ploughs and selection of most suitable types and their adaptation to local conditions; testing of ridge ploughs and the design of a new light steel ridger at less than 1/3 of the price of those previously available; testing of Persian wheel type of water lifts and

the development of an improved design; draught and road speed tests of rubber-tired carts and the design of cart bodies for rubber-tyre equipment; development of Burmese type wet land puddling implements; testing of engine and bullock driven cane crushing mills and the design of improvements to bullock power mills; development of an improved method of hitching draught animals by means of leather harness; improvements to earth-scoops; testing of indigenous handfed seed drills and the design of a mechanical seed distributing attachment for the indigenous drill; the design of a new device for polishing turmeric, an improved water lift of circular mhote type, a new device for forming bunds; improved ball and roller bearing mhote wheels of higher efficiency at lower cost; simple mechanical seed drill for sowing any seed at any desired seed rates with adjustable depth of sowing; a new grain polishing and cotton seed defibrating machine; a new guntaka or blade harrow; improved cotton stalk puller; improved pitting crowbar; improved cast iron grating for jaggery furnace; clod crushers, etc., etc.

### ASTRONOMICAL NOTES.

**Planets during November 1937.**—About the end of the month, Mercury will be visible in the western sky for a short while after sunset. Venus is gradually moving towards the Sun but will still be a fairly bright object rising about an hour and a half before sunrise.

Mars will be situated in the western sky in the early part of the night and is getting fainter. Jupiter also can be seen nearly in the same direction a little to the west of Mars. The stellar magnitude of the planet at this time will be  $-1.6$ ; the same as that of Sirius.

Saturn is moving in a retrograde direction; it will cross the meridian at about 8 p.m. in the middle of the month and will be in a convenient position for observation. Uranus will be in opposition to the Sun on November 4 and will be just visible to the naked eye as a faint star very near  $\alpha$  Arietis.

The only lunar eclipse of 1937 occurs on November 18; but it will not be visible in India. It is a partial eclipse, of magnitude 0.15.

**Comets.**—Finsler's comet (1937 f) became fairly bright in August and has been widely observed. From the photographs taken, the comet appears to have developed several tail streamers in a fan-shaped form, the brightest tail being about  $9^\circ$  in length. It is moving farther away from the earth and getting fainter.

According to a U.A.I. circular, Encke's comet has been re-discovered by Jeffers at the Lick Observatory. It was an extremely faint and diffuse object at that time and had no central condensation; its estimated magnitude was 18.

**A Supernova.**—Information has been received from the Harvard College Observatory, of the discovery by Dr. Zwicky on August 28, of a bright supernova of magnitude 8.5 in the nebula Index Catalogue No. 4182, in the constellation Canes Venatici. By September 8, the star appears to have declined one magnitude in brightness. Prof. Seares has announced that spectrograms obtained on August 29 by Humason at Mt. Wilson show the typical supernova bands.

T.P.B.

## CENTENARIES

S. R. Ranganathan, M.A., L.T., F.L.A.

University Librarian, Madras

### Neumann, Kaspar (1683-1737)

**K**ASPAR NEUMANN, a celebrated German Chemist, was born at Zullichere, July 11, 1683. After receiving his education in his native country, he travelled in England, France, Holland and Italy and visited the famous chemists of his time. On his return in 1721, he was appointed Professor of Chemistry in the Royal College of Physics and Surgery at Berlin. He also became a Fellow of the Royal Society, London.

#### HIS PUBLICATIONS

In 1725, he sent his first paper to the *Philosophical transactions* under the title *On camphor*. In this paper, he showed that "camphor is a substance differing in its properties from oils, resins, volatile salts and gums; that is in fact a *sui generis* substance; and that it is obtainable from thyme and perhaps from some other vegetables, besides the so-called camphor-tree". He wrote several other papers, whose substance was all incorporated in a posthumous publication entitled *Chymia medica dogmatico-experimentalis*, etc., which was edited and published in four volumes by Ch. H. Kassel in 1749-55. An abridged English translation of this work was brought out by Lewis in one volume in 1760 and in two volumes in 1773. It was also translated into several other European languages.

#### BEGINNINGS OF BIOCHEMISTRY

A contemporary estimate of his work is that it exhibited "a better view than had before been given by any other writer, of all that was then known in chemistry. They, moreover, contain many new analyses made by the author himself of certain medicinal and alimentary substances; such as amber, opium, castor, tea, coffee, etc.". He also examined the "acid juice of ants and showed (what has been confirmed by

subsequent experiments) that it coincides in its leading properties with the acetic acid".

Neumann died, October 20, 1737, at Berlin.

### Woolf, Arthur (1766-1837)

**A**RTHUR WOOLF, mining engineer, was born at Camborne in Cornwall in November 1766. His father was a carpenter and he himself was apprenticed to a carpenter in his native place. But he soon migrated to London and by 1795 he became a master-engineer. In 1796 he went to assist Jonathan Hornblower in repairing a two-cylinder engine at Meux's brewery. This led to his employment as the resident engineer of that brewery, where he remained till 1806.

#### WOOLF-ENGINES

He had already made small improvements in steam engines and took out some patents. In 1806 he became a partner with another engineer, who owned a steam-engine factory at Lambeth. In 1810 he took out the most important of his patents which related to the compound engine. Using steam of a fairly high pressure, and cutting off supply before the end of the stroke in the small cylinder, Woolf expanded the steam to several times its original volume. The compound engines which discharge steam directly from the high to the low pressure cylinders without the use of an intermediate receiver are called Woolf-engines.

Woolf introduced his engines widely as a pumping engine in the mines of Cornwall. They held the field for about twenty years and were then superseded by Trivithick's high-pressure single-cylinder engine, which was similar in construction.

Woolf died, October 26, 1837.

## RESEARCH ITEMS.

**The Experiment of Sagnac and the Theory of Relativity.**—In the original experiment of Sagnac (*Comptes Rendus*, 1913, 157, 708 and 1410) a flat circular disc, capable of rotation about an axis passing through its centre, has three mirrors fixed so as to be tangential to the disc at the three corners of a square inscribed in the circle. At the fourth corner there is a half-silvered plate P, parallel to the mirrors at the two adjacent corners. A source of light fixed to the disc sends a ray of light inclined at  $45^\circ$  to P and the reflected and transmitted rays are reflected by the three mirrors so as to travel along the sides of the inscribed square, but in opposite senses. The two rays are again brought together and form interference fringes which are photographed by a camera also fixed to the disc. When the disc rotates with an angular velocity  $\omega$ , there is a fringe-shift equal to  $4\omega R^2/c\lambda$  fringes, where R is the area of the inscribed square and  $c$  and  $\lambda$  are the velocity and wavelength of the light employed. Now A. Dufour and P. Prunier have repeated the experiment with some modifications (*Comptes Rendus*, 1937, 204, 1322 and 1925). They use a source fixed to the rotating disc, as also a source fixed outside the disc and thus not rotating with it. In each revolution the photographic plate is illuminated for only a short time of the order of  $10^{-5}$  sec. They find that the fringe-shift is the same (within an error of 15%) both when the source is fixed and when it is rotating. Next they remove the camera also from the disc and fix it to a wall in order to find out the effect observed by a fixed observer. There is a secondary fringe shift due to the rotation of the interferometer in the finite interval ( $10^{-5}$  sec.) of illumination; but the effect of this is eliminated by finding the fringe-shift in two positions of the plate P which are symmetrical on either side of the position it has when the central fringe occupies the whole field of interference and taking the mean of the two Sagnac effects found. The result was that they obtained the same fringe-shift as when the camera was fixed to the rotating disc, within an error of 5%. They thought that according to the theory of Relativity there should have been a difference in the two cases and therefore reported that their results were against that theory. Now Langevin (*Comptes Rendus*, 1937, 205, 304) has shown that their interpretation of the theory of Relativity was not correct and that the identity of the fringe-shifts when the camera is fixed and rotating is in entire accordance with Einstein's Theory.

T. S. S.

**Molecular Beams as Spectroscopic Sources.**

—On account of the Doppler width associated with ordinary sources of light, the structure of close groups of lines cannot be found by means of such sources. If a beam of molecular rays is made to emit light in a direction perpendicular to the beam, the Doppler effect is minimised and very narrow structures can be resolved. Dunoyer (*Comptes Rendus*, 1913, 157, 1068) excited the molecular beam by illuminating it with its resonance radiation. Jackson and Kuhn [*Proc. Roy. Soc.*, (A), 1935, 148, 335] used absorp-

tion by the molecular beam. Both these methods are of very limited application being confined to a few lines of the spectrum. Now K. W. Meissner and K. F. Luft (*Ann. der Physik*, 1937, 23, 667; *Sitzb. d. Königl. Preuss. Akad. d. Wiss.*, Berlin, 1937, 12; *Zs. f. Phys.*, 1937, 106, 362) have excited the molecular beam by electron impacts; by increasing the electron current and the vapour pressure of the molecular beam near the furnace, and also increasing the thickness of the cross-section of the beam, they have made this source bright enough to give good patterns in 1½ hours with a two-prism spectrograph (two Rutherford prisms employed. Aperture  $f/17$ ) and a Fabry-Perot interferometer having distance pieces upto 18 cm. With this apparatus they have been able to measure wave-lengths to four decimal places and determining such small separations as the intervals of the D and F terms in sodium and potassium. They have also observed the hyperfine structure of the resonance lines of potassium and find separations agreeing with those calculated by Rabi and co-workers by the magnetic deflection method. They also find, in agreement with these authors, that the magnetic moment of the potassium nucleus is positive. Jackson and Kuhn, whose original researches were thus contradicted by these results, have now repeated their experiment (*Nature*, 1937, 140, 276) and confirm the results of Meissner and of Rabi, and also give an explanation for their previous finding.

T. S. S.

**A Photoelectric Method of Measuring pH with Indicators.**—A photoelectric method of measuring light absorption for precise determination of pH value with indicators has been developed by G. F. Lothian (*Trans. Farad. Soc.*, 1937, 33, 1239). For common indicators, variation in pH causes change in density of absorption band, the change being greatest at the peak of the band. For measurements of absorptions the Hilger Spekker photoelectric absorptiometer in conjunction with a suitable light filter is used instead of the visual, spectrophotometer. The calibration curve of variation in density of absorption and pH is drawn for the indicator. The mean precision in pH measurement varies from 0.02 to 0.01 for different indicators. Extension of the method to determination of pH of coloured solutions is also possible. The method avoids the necessity for maintaining standard solutions for matching the test solutions, is independent of visual judgment of colour match, and is capable of high accuracy of measurement even with a small quantity of the indicator.

K. S. RAO.

**Estimation of Essential Amino Acids in Proteins.**—Two contributions of particular interest to protein chemists have recently been published (*Biochem. J.*, 1937, 31, 1390, 1422). In the first paper, Bailey has reviewed the different methods for the estimation of cystine and recommends Lugg's modification of Sullivan method as a specific method, provided the



cystine content of the protein is greater than 0.5%. Lugg's modification of Folin-Merenz method is advocated for the determination of total disulphide. The factors responsible for the errors in the cystine determination are: (1) inhibition of colour due to extraneous reducers and (2) losses occurring during hydrolysis, due to deamination, decarboxylation or condensation of cystine with substances of an aldehydic nature. The hydrolysis of proteins in presence of carbohydrate results in the production of large amounts of S- containing humin involving considerable destruction of cystine. In the second paper, Lugg has recorded the results of his investigations on the effects of extraneous substances on the Millon reaction for tyrosine and this has led to a satisfactory method involving a radical change in the Folin and Ciocateau procedure. Mercuration of the tyrosine and precipitation of tryptophane is carried out in one step and the reaction mixture is diluted with the mercuric salts reagent. With this method there is no appreciable error in presence of 0.25 milli equiv. of chlorides, 3 millimol. NaOH, 1 millimol.  $ZnSO_4$ , 100 mg. glycine, 30 mg. glycine + 10 mg. phenylalanine, 1 mg. histidine or 5 mg. methionine. There is no interference due to the presence of carbohydrates. The colour reaction between nitrous acid and tryptophane mercurial has been made the basis of a very delicate and simple colorimetric method for the estimation of tryptophane.

**Simplified Volumetric Determination of  $\alpha$ - $\beta$ - and  $\gamma$ -Cellulose in Pulps and Papers.**—Herbert F. Launer. (*Journ. Res. of the National Bureau of Standards*, 1937, 19, 333) describes simple and rapid volumetric method for the determination of  $\alpha$ -,  $\beta$ - and  $\gamma$ -celluloses. Details are given of the procedure for (a) mercerisation and filtration, (b) treatment of the  $\alpha$ -cellulose and (c) treatment of the  $\beta$ - and  $\gamma$ -portion and finally of the  $\gamma$ -portion as well. The methods of calculation of the total cellulose content and those of  $\alpha$ -,  $\beta$ - and  $\gamma$ - celluloses respectively, are illustrated by an example.

The merits of the method consist in (1) avoidance of moisture and ash determinations and (2) the employment of small samples ranging from 0.03–0.3 g., thereby ensuring rapidity of working.

The results obtained by this method are shown to be fully as accurate as those obtained by the more tedious gravimetric methods.

K. R. K.

**Origin and Movements of Magma in a Strong Earth.**—It is commonly assumed that a continuous shell of weakness underlies the crust, and that this zone of weakness controls the movement of magma during isostatic adjustments. S. Delury (*Am. Journ. Sci.*, 1937, 34, No. 201) who of late has been devoting considerable attention to the study of the mechanics of the Earth's crust, has just put forward his conception of a 'Strong Earth' except where regions are locally liquefied. Basing his arguments on such a conception,

he believes that movements of the magma are the direct cause for all Earth movements.

From a detailed study of the development of heat through radiothermal energy, he shows that the distribution of thermal gradients favours the idea of an abrupt change of temperature in vertical rather than in horizontal directions. From this, he has deduced that initially magmas are generated as a thin sheet horizontally disposed. Melting of rocks due to additional temperature increases the volume, and the overlying formation bends elastically and finally ruptures. This brings the magma to shallow regions. This concept of a strong Earth explains properly the development of magmas and their forcible migration to higher levels, a phenomenon which is so closely connected with Earth movements.

**A Study of the Actinian *Phytocoetes gangeticus*** (Zool. Jahrb. Abt. Anat. Ont., 1937, 62, 395–422).—The brackish-water anemone *Phytocoetes gangeticus* first described by Annandale and so far known only from the Gangetic Delta, has been investigated in detail by Kesava Panikkar, from material obtained at Madras. The mesenterial and tentacular arrangements of the Actinian follow the typical plan. Most of the specimens have six pairs of macrocnemes and two other orders of microcnemes with four sets of tentacles, while a few have an incomplete fourth order of mesenteries and fifth cycle of tentacles. Acontia are present on the older couples of macrocnemes and the acontial cnidæ include both penicilli and spirulæ. The distribution and degree of development of acontia and gonads on the different mesenteries correspond to the order of succession of macrocnemes. Mesenteries of the fifth and sixth couples are weaker than others. The tentacles, filaments and acontia appear early in development. The post-Edwardsia stages seem to be prolonged and many of the adult features appear before all the primary mesenteries have developed. The presence of ovaries in the mesenteries of specimens in the Edwardsia stage strongly suggests the occurrence of neoteny in the anemone. Accounts of the habits, habitats and distribution of the anemone are given. The structural and developmental details, the systematic relationships of the anemone and the question of neoteny are discussed at the end of the article.

**Malabar Prawn Industry.**—The current number of the *Journal of the Bombay Natural History Society* contains a study of the Malabar prawn industry by Kesava Panikkar. After giving a general account of the prawns of Travancore with special reference to their habits, the fishing operations now in vogue are described and illustrated. Accounts of curing and marketing of prawns are given. The economics of the industry is examined in the light of available data. The question of improvement of the industry is discussed and the necessity for superior methods of preservation, planned production, improved marketing facilities, co-operative enterprise among those engaged in the industry, and biological research, is emphasised.

**Agricultural Research in India.**

"THE Annual Report of the Imperial Council of Agricultural Research for the year 1936-37" which has just been published, with commendable promptitude—a fact which considerably enhances its value to the general public—is a record of yet another year of strenuous and intensive work. The work of the Research Council embraces, it may be recalled, not merely problems relating to scientific agriculture but also to its practical and economic aspects which so materially limit the results of scientific research. Comprehensive as the various lines of the work have been in the past the report discloses that advance has been made along a much wider front than before; in fact so greatly have the activities multiplied that it is just as well that the Council should have thought it necessary to conduct a kind of stock-taking. For this purpose, the Council have invited Sir John Russell and Dr. Wright to examine the situation and advise regarding the lines of future progress and their visit to India for this purpose has been one of the outstanding events of the year. Their report will soon form the subject of discussion and consideration by the Advisory Body of the Council; many lines of the work already in progress and the results achieved have won their approval and appreciation and we have no doubt that their report besides being greatly helpful will bear more ample testimony to the excellence of the aims, methods and results.

The section on Animal Husbandry has greatly expanded its activities and bids fair to even outstrip the other sections—quite a contrast with the state of affairs some years ago—thanks to the great interest evinced by His Excellency the Viceroy in the welfare of the cattle of India. The second Meeting of the Animal Husbandry Wing of the Board of Agriculture and Animal Husbandry which was held in December 1936, was an important event and the discussions embraced many important matters such as Veterinary Education, Animal Health and Breeding, Nutrition and Dairying. The report details briefly the decisions reached on these important matters, among which we may mention the one recommending more attention to the development of the various breeds of buffaloes as dairy animals, the formation of Fodder and Grazing Committees in the provinces to be co-ordinated by the Imperial Council, the progress made in the definition of important breed characteristics of Indian dairy cattle for the maintenance of Pedigree Herd Books, the proposals for opening a Central Veterinary College for the highest grade of veterinary education and the progress made in respect of the research schemes conducted by the Cattle Disease Investigation Officers appointed under this scheme. A Village Economic Enquiry on the production and consumption of milk was completed in the year and we look forward to the publication of the report of this enquiry which will furnish the economic background for the working out of a sound general policy for the improvement of cattle in India.

The Research schemes in respect of the various crops are dealt with briefly and the salient features indicated. Most of these schemes which had completed their original periods of sanction

were given further extensions to avoid any break in the continuity of the work pending the report of Sir John Russell. Sugarcane and sugar come in for the largest share both in the number of research schemes and the amount of expenditure incurred, a fact fully warranted no doubt by the magnitude of the industry in India. We note that the comprehensive scheme for enquiring into the cost of production of crops has come to a close and the report is under preparation. This should be a veritable mine of information on the economic side of farming in most parts of India and its value will probably relate even more to these particular features than to the cost of production of sugarcane itself in connection with which the inquiry was initiated. The various Sugarcane Research Stations have all continued to work along the same lines as heretofore. Manurial trials in U.P. indicated 100 lbs. of nitrogen per acre as the limit of profitable application for sugarcane while experiments in the Bombay-Deccan show that even at 300 lbs. per acre the optimum dose has not been reached and doeses up to 600 lbs. per acre are being investigated. Cane-breeding in Mysore demonstrated the possibility of using X-rays for the production of a number of new bud variations; the Coimbatore varieties demonstrated their adaptability in all the stations, and one of them namely Co. 419 has given an out-turn of 54 tons per acre. The sugar section of the Harcourt Butler Technological Institute has been converted into the Imperial Institute of Sugar Technology, the cost to the Central Government being estimated at Rupees 14 lakhs to be spent over a period of five years. As a teaching and research Institution in Sugar Technology we hope the Institution will develop into one of the foremost institutions of the kind in the world. We note among the research items of the Institute reference to more than one method of utilisation of molasses including the recovery by chemical means of all the valuable ingredients. Let us hope that practical methods will be devised to work it successfully, for this method of molasses treatment cuts the problem at the very root. In connection with its utilisation as a cattle feed, feeding trials are in progress with six different kinds of feed mixtures. Obviously in a country where the deficiency of cattle feeds is a chronic and crying problem this method holds out probably the greatest promise.

Horticultural Research occupies an important place among the year's activities and has related not only to problems of cultivation but to storage and preservation. It has been demonstrated that many of the choice varieties of the mango give promise of good keeping quality in cold storage and that fully ripe and yellow Nagpur oranges can be kept in good condition for three months in cold storage. The subject of gas storage of fruits and vegetables was also considered and an officer deputed to Cambridge for training in the technique of this method. In the U.P. fruit station it has been found that two of the East Malling apple stocks reputed to be resistant to woolly aphids have proved to be vigorous growers and to maintain their resistant quality. In the Punjab, a scheme for the preservation of fruit and vegetables was

being worked and good progress made in the preparation of Citrus squashes, Cordials and Tomato Ketchup, while work on the canning of fruits and vegetables, drying and other methods has been in progress. Important work in fruit culture, canning and fruit preservation are foreshadowed for the fruit research stations in the N.W. Frontier Provinces and Baluchistan. Let us hope that many of these will prove a much-needed ally to the Indian Sugar Industry, in regard to which the spectre of overproduction is already in sight, by affording a new outlet for sugar. The important subject of pests and diseases especially of the Citrus have been the subject of research in the Punjab and the N.W. Frontier Provinces in the latter of which a survey of the insect pests of fruit trees with special reference to the Sanjose Scale is in progress. Work in the former indicated that Chlorosis can be controlled by the injection or spraying with highly dilute ferrous sulphate solution.

The subject of dry farming, important over a large section of the country, is now being studied in five stations in the Bombay, Hyderabad and Madras provinces, and the problems of runoff, penetration, and underground moisture have been intensively studied. The loss of soil due to run off in unprotected fields in the black cotton soil tract in Sholapur is put down at the amazing figure of 115 tons per acre after one or two days of heavy rainfall. Considerable practical value is claimed for the Bombay system of dry farming tried in these stations, and the method can perhaps be now recommended for general adoption. Soil research has related to many fundamental problems, nitrogen fixation, colloid constituents of soils, the relation of soil moisture to crop yield, the organic constituents of soils; the subject of photofertilisation on which views are divergent is being further pursued, as well as, that of soil nitrogen increase due to the application of molasses and other carbonaceous substances to the soil. In respect of wheat, provision for the establishment of a milling and baking laboratory at Lyallpur is a noteworthy development. Quality in rice, the malting of cholam, fairly extensive work on oil seeds both in the research stations and on the technology of vegetable oils in the Harcourt Butler Technological Institute, the cultivation of medicinal plants and of pyrethrum, the breeding of fresh-water fish in Bengal, potato breeding experiments, rust, research on wheat and other matters of research have continued to receive attention. Locust Research which is one of the major activities of the Council has continued its many-sided attack on the problem and it is now proposed to transfer the work to the Government of India, probably as a permanent organisation.

On the economic side certainly the most important section has been that of Agricultural Marketing. The surveys with which this section commenced to work have been completed in respect of all the main commodities. Several new commodities were also included in the list during the year and the main surveys in most of the provinces were completed. The Report on Wheat has already been published and others are said to be in an advanced stage of preparation. We would suggest the publication without

delay of the various provincial surveys, for, irrespective of the final action which the Council may take the surveys will certainly interest the trade in general and the *entrepreneur* in particular who may meanwhile be expected to utilise the information in a manner calculated to improve the trade and production in these articles. A measure of great practical importance in marketing is the passing of the Agricultural Produce Act of 1937 by the Central Legislature; rules prescribing grade designation, definitions of quality, methods of marketing, packing, etc., for tobacco, grapes, eggs, hides and skin were issued under the Act and the Stamp "Agmark" either alone or inside the map of India has been adopted as the "national mark" for graded produce. It is essential, we think, that the public should be apprised of the superiority of such graded produce so that it may fetch a higher price in the market and thereby bring about a general resort to this improved trade method. Without the incentive of a higher price it will be useless to expect any general adoption of this practice. We would suggest that a special advertisement campaign with regard to this kind of produce should be carried on simultaneously. Having had occasion to personally inspect the egg grading station in Travancore we would extend a special meed of praise to this work. One of the most important developments in the year is the action taken for affording cold storage facilities on a large scale, the initiative having been taken by the Army Department. The marketing section of the Council have actively co-operated and it is very gratifying to know that a chain of such cold storage depots will soon be erected in all the important stations in Upper India. Worked in conjunction with cold storage railway vans for the transport of perishable produce this new development will afford most substantial help to the grower of all kinds of perishable produce and in welcoming the development we will plead for the erection of similar depots in some of the large South Indian centres also.

The Publication Branch has in addition to the three journals *Agriculture and Livestock in India*, *Indian Journal of Agricultural Science* and *The Indian Journal of Veterinary Science and Animal Husbandry* brought out quite a useful "Handbook of Statistics for use in plant breeding and agricultural problems" and a number of miscellaneous bulletins. We also note more than one new feature in the *Agriculture and Livestock in India* especially the series of popular articles. The report is a comprehensive summary of the work done on a very large number of subjects. Each one of these is of great interest and importance to Indian Agriculture and in a brief review one could obviously do little more than touch upon a point here and a point there. The report must be read to realise the very wide and rapidly expanding scale on which schemes of agricultural improvement are being planned and worked by the agency and with the funds mainly of the Central Government as distinguished from the activities of the Provincial Governments.

A. K. Y

## Biochemical and Allied Research in India.\*

THE Society of Biological Chemists, India, was founded some six years ago and has since been doing excellent work. Its activities have now extended all over India, with branches or representatives at all important scientific centres. In addition to holding scientific meetings and publishing half-yearly proceedings and occasional monographs, the Society also issues annual reviews of progress in Biochemistry and allied subjects which are now recognised both in India and abroad. The present publication is the seventh of the series.

The reviews have been classified under seventeen main heads and have contributed by authors, all of whom are specialists in their respective subjects. The majority of the sections relate to agriculture and kindred subjects in which a large volume of work is being done in India. Human physiology, foods and nutrition are also given the necessary prominence and it may reasonably be expected that, in the course of the next few years they will attract even more workers than they do at present.

A number of useful contributions have been made to Enzyme Chemistry, but most of the papers referred to in that section have come from only two or three laboratories. The subject is one of considerable importance and it is hoped that it will soon attract workers in other laboratories as well. Similar criticism would also apply to Protein Chemistry, which is also being studied only in a few laboratories. Vitamins have attracted much attention, but mostly on the analytical side. A few researches of fundamental interest have recently been started and it is hoped that many more will soon follow. Very little work has been carried out on hormones and plant stimulants. These are important subjects and should attract at least a few of the leading workers in the country. As in previous years, researchers in Pharmacology are mostly confined to a few laboratories in North India. This is very disappointing when considering that, many of the Universities and Medical Colleges have created Chairs for that subject and have provided the necessary equipment. If the Professors are hampered by much teaching and other routine, they should be relieved of them as far as possible and given more scope for research. Much work has been done on human Pathology and Bacteriology, most of the research being sponsored by the Indian Research Fund Association. Malaria, Cholera, Plague, Kala-azar and Leprosy come in for special study. Researches on the related parasites, intermediate hosts and carriers have also been extended. Human Physiology is drawing increasing amount of attention and it is hoped that, in a few years, still more work will be done in that subject. In spite of their very great practical importance, Microbiology and Fermentation have attracted very few workers, most of the research being confined to only

one or two laboratories. This is indeed very disappointing. Chemistry of Plant Products provides a common ground for both organic and biological chemists and has naturally attracted a number of workers. Most of the researches are essentially of analytical character, but it is hoped that, before long, enquiries of more practical value will be undertaken. Researches on Plant Physiology are mostly from one laboratory, but it is rather doubtful whether the reviewer has done justice to all the researches on plant nutrition in different parts of the country. A number of publications relating to Agronomy and Agricultural Industries have been issued, but most of these are of a miscellaneous character. It will be difficult for a casual reader to make out as to how far they have assisted in the related industries. Researches on Soils, Manures and Fertilisers have continued to attract a number of workers but much of the work is essentially of an academic character. More attention should be directed to the practical application of the various findings. Phytopathology, which has been divided into two sub-divisions—Mycology and Entomology—refers to a number of interesting publications. Most of the work is of the systematic type, which though of considerable scientific value, does not carry much practical relief with it. With more concentrated effort, it should be possible to successfully control many of the plant diseases and pests which are now rampant in India. The amount of work done in Dairy Chemistry is pathetically small. It is to be hoped that the recent appeal of His Excellency the Viceroy will evoke more response and a larger number of workers will devote themselves to that subject. A central research laboratory devoted to the study of dairy products is also badly needed. Very little research work has been done in animal nutrition. With the exception of a few papers in the *Indian Journal of Veterinary Science*, practically no original work appears to have been published during the period under review. The slackness in this line is probably due to the shifting of the Imperial Physiological Chemist's Section from Bangalore to Izatnagar and it is expected that much valuable work will come out in the next review. Soil Physics has been mostly confined to one or two laboratories. It is probably due to paucity of trained workers. A similar criticism would also apply to Agricultural Meteorology in which only one laboratory is now interested. This defect can be overcome by either training more workers or establishing a number of sub-sections in different parts of the country.

If one may institute a comparison, the present publication may be quite properly described as the biggest and the best of the series issued by the Society. Considering the price, the paper and the printing are quite good. The thicker cardboard cover is an improvement and makes the copies more solid and lasting.

By bringing all the biochemical and allied work done in India in one compact volume, the Society is doing two-fold service. In the first place, such publications present critical

\* *Review of Biochemical and Allied Research in India*, Vol. 7, 1936. Compiled and published by the Society of Biological Chemists, India. (Office : Indian Institute of Science, Bangalore.) Pp. 164; Price Rs. 2, or 3s. net.



reviews of the progress made from year to year. Secondly, they offer a useful bibliography of the work done in the whole country (and by Indian workers abroad) so that even out-station workers with no library facilities can keep in touch with the latest developments.

The publication is not without its defects. In the first place, it may be pointed out that there is considerable overlapping of matter between different sections. This is partly due to the creation of a number of independent sections relating to closely allied branches and partly owing to the fact that the contributors who are derived from different parts of the country have no means of consulting each other. This defect can be overcome by appointing small editorial committees to scrutinise all the publications both independently and collectively. A second observation that one may make is that many of the sections are more of the nature of abstracts than of reviews. Abstracts are undoubtedly very useful but the publications cannot, in that case, be called reviews. Certain amount of selection in regard to the matter is needed. Some criticism—in a kind and

helpful spirit—will also add to the value of the contributions. Many of the reviewers have cited reference to unpublished work—done by themselves and their friends—which, though useful, is not quite desirable in practice. Such a procedure will not be fair to the other authors who do not possess a similar advantage. Some of the contributors refer freely to their departmental reports, *Proceedings of the Indian Science Congress* and *Proceedings of the Society of Biological Chemists, India*—which cannot be classed as original publications of completed work. Many of these reports are essentially of a preliminary character and should have been left out until they are published in specialist journals in more complete form. The indices are not complete. A wider choice of 'subjects' will be helpful to most of the readers. The author index does not refer to all publications cited in the text. These are all small and inevitable defects in new ventures of this type and it is hoped that they will be steadily eliminated from later publications.

V. SUBRAHMANYAN.

## Recent Developments in Indian Geology.\*

PROFESSOR WADIA, in the course of his address, dealt with certain branches of Indian geology in which marked progress was achieved during the last two decades. Among the main lines of advance is the progress towards the unravelling of the most ancient rock-complexes of India carrying the principal ore-deposits of the country, in which Sir L. Fermor, Dr. Heron and the Mysore State Geologists have taken a leading part. Their classification, origins and structural characters are now better understood. It is in the steadfast pursuit of pure research in the problems of rock and ore origins that there lies the best chance of achieving results of economic value and industrial utility. The detailed study of the Gondwana system of rocks, the carrier of the coal-deposits of the country is proceeding, the principal contributions being those by Dr. Fox on the stratigraphy and correlation of the scattered Gondwana basins, and on the total coal reserves in them, and by Prof. Sahni on the study of fossil vegetation. Geologists have succeeded in proving during the late years that the thick pile of lavas building the Deccan plateau was erupted

in early Tertiary age rather than in late Mesozoic. A substantial body of the evidence for this belief has been collected by the research workers of the Lucknow, Benares and Mysore Universities,—a welcome sign of the time of increasing co-operation between the official department and universities. The most significant advance during the last 15 years is in our knowledge of the Himalayas, recent work on the structure, origin and age of these mountains by Pilgrim, Wadia, West and Auden has materially changed old ideas. In Kashmir, Simla and Garhwal Himalayas enormous tangential thrusts have been proved whereby large slices of the mountains have moved forward for miles, piled up on each other and folded back. These great earth-movements, in the Punjab Himalayas at least, are now proved to be of so geologically recent a date that Early Man must have been a witness to the finishing uplifts of the mountains.

The value of the total mineral production of India has been doubled in the last 25 years and the Geological Survey of India is devoting more and more attention to economic, engineering, soil, water-supply and industrial problems than in the past.

The President briefly reviewed the progress of Palaeontology in India and welcomed the growth of the study of fossil plants and animals in the universities.

\* Presidential Address at the Annual General Meeting to the *Geological, Mining & Metallurgical Society of India*, by Dr. D. N. Wadia, President of the Society, 30th September 1937.

## SCIENCE NOTES.

**Chemical Industries in India.**—One of the main foundations of successful chemical industries is a cheap supply of sulphuric acid. India lacks any indigenous source of sulphur of commercial size and up to the present no use has been made of the sulphide ores occurring at Bawdwin in the N. Shan States or at the copper mines in Bihar. Schemes have, from time to time, been formulated for the purpose, but have never been brought to fruition. India is therefore dependent upon imported sulphur for its supplies of this most important acid. Imports of sulphur in 1935-36, amounted to 26,000 tons and of sulphuric acid to 284 tons. The output of the acid plants in the country is a little over 31,000 tons of 100 per cent. acid. The manufacture is widely distributed, and is a healthy sign of growing activity in the chemical industries. The objects of manufacture are varied. In Bihar, the acid is largely used for the preparation of ammonium sulphate from the coke by-product recovery plants and in the tin plate works; in Burma, for refining oil products and in the Nilgiris for cordite. The output of ammonium sulphate amounted to 15,400 tons in 1935. Fairly large quantities of aluminous sulphates and alum are produced by treating the indigenous bauxite with sulphuric acid.

Saltpetre is produced in Bihar, the United Provinces and the Punjab by the laxiviation of nitrate bearing efflorescence formed near village sites after treatment with wood ashes. The crude product requires refining before use. The production amounted to over 12,600 tons in 1935. Although some is utilised as a manure and for gunpowder, the greater part is exported, the exports in 1935 being a little over 8,800 tons.

Magnesium chloride is produced from the natural bitterns of the Rann of Cutch and the Gulf of Cambay. The material is of high grade and has almost completely ousted the imported German product. There is also a small export trade.

Throughout India, use is made of the saline efflorescence occurring for the production of impure varieties of soda and similarly from the alkaline lakes in Sind. Some ten years ago a large soda factory was built in the Indian State of Dhorangadhra on the little Rann of Cutch. The Shri Shakti Alkali Works were intended to produce annually the equivalent of 22,000 tons of sodium carbonate by the ammonia soda process. Attempts to commence production in 1928 and subsequently, proved abortive. The Magadi Soda Works which had a plant near Calcutta for producing caustic soda from carbonate imported from the Magade Lake in Kenya went into liquidation about 12 years ago. There is hope that various soda products will shortly be made in India by the Imperial Chemical Industries, Ltd. Imports of soda salts amount to 69,000 tons per annum. (*The Chemical Age*, 38, No. 932, 410.)

**I. C. I. Chemicals in India.**—Imperial Chemical Industries (India), Ltd., which has for many years played a large part in the import of industrial chemicals for the Indian market,

announces its intention to float an Indian company for the local manufacture of products essential to Indian industrial development.

Factories will be erected in the Punjab for the manufacture of soda ash and in Bengal for the manufacture of chlorine and caustic soda, and further plans will be developed later. The company will have the full technical support of Imperial Chemical Industries, Ltd., London, in these developments.

It is intended that a large proportion of the capital shall be offered for subscription by the Indian public. Indian labour will be employed, and Indian Staff will be trained to share in technical management.

At the General Meeting of Imperial Chemical Industries, Ltd., held in London, in April last, Lord McGowan stated that Mr. H. O. Smith, one of the Directors, had been to India, where the company had considerable interests, in alkali, dyes, explosives, general chemicals, and metals, and that the continued progress of that country and the development which was to be expected under the new scheme of self-government, fully justified a fresh general survey of the possibilities.—(*Chemical Age*, 1937, 37, No. 947.)

**Herman von Helmholtz.**—*The Bausch & Lomb Magazine* for August 1937, contains a brief sketch of the life of Helmholtz, pioneer in Physiological Optics, by Everett White Melson. In the history of Physiological Optics, Helmholtz, discoverer of the Ophthalmoscope, stands out as the most outstanding figure. "He investigated the optical contents of the eye, measured the radii of curvature of the crystalline lens for near and far vision; explained the mechanism of accommodation and discussed the mechanism of colour vision applying his theory to the explanation of colour blindness." He was born at Potsdam, Germany, on August 31, 1821, and graduated in medicine in 1842 from Friedrich Wilhelm Institute. He became famous as a teacher and lectured on Physiology, Pathology and Anatomy at Königsburg, Bonn and Heidelberg. In 1871, he became Director of the Physical Institute at Berlin, and in 1877, the Director of the Physico-Technical Institute. His researches were not confined to Physiological Optics alone; in the field of Physiological Acoustics, he published "His Sensations of Acoustics", explaining the mechanism of the bones of the ear and the action of the cochlea on the principles of sympathetic vibrations. He propounded the doctrine of the conservation of energy, and his theory of the atomic nature of electricity had far-reaching consequences. He inspired the experimental work of Hertz which proved the existence of Maxwell's electromagnetic waves, thus opening the way to wireless telegraphy.

In 1831, Helmholtz attended the World's Fair at Chicago. During his return trip to Bremen he fell down the companionway of his ship, sustaining injuries which led to his death in 1894.

**Nutrition in Relation to Health, Agriculture and Economic Policy.**—The League of Nations has just issued an authoritative and comprehensive report on Nutrition, as a result of two years' work by an International Committee of agricultural, economic and health experts working under the auspices of the League. The report is concerned mainly with the economic aspects of nutrition policy and with its relation to agriculture. A chapter on the physiological aspects of the problem is also included. The report is divided into 3 parts; the first part gives a general survey of the problem and of the work already carried out. The second part is exclusively devoted to the health aspect of nutrition and the third part to a detailed examination of the economic and agricultural considerations connected with nutrition policy. The report concludes with a collection of evidence relating to the present state of nutrition in various parts of the world. "The malnutrition which exists in all countries is at once a challenge and an opportunity; a challenge to men's consciences and an opportunity to eradicate a social evil by methods which will increase economic prosperity." The report contains 327 pages, and is priced 7sh. 6d.

**Broadcasting in India.**—An outline of the Broadcasting policy and plan for India, has been published in *The Indian Listener* (July 1937). The Government of India has authorised an expenditure of Rs. 40 lakhs and this sum has already been allocated for expenditure on different projects. At the outset it may be mentioned that the "All India Radio" has set itself the task of providing a satisfactory broadcasting service to the whole country. To achieve this end, over the vast area, the basic principle adopted is to provide a short-wave service to the whole country and to support this by a continual expansion of the area served by medium-wave stations as funds become available.

4 short-wave key stations (10 k.w.) will be located at Delhi, Bombay, Calcutta and Madras. A second short-wave transmitter (5 k.w.) will also be provided at Delhi for special purposes. The development programme does not envisage any future increase in the number of short-wave stations. These short-wave stations will provide a "second grade service" to the whole of India. Five medium-wave stations will be located at Lahore, Lucknow, Trichinopoly, Decca (each 5 k.w.) and Madras (250 watts) with these stations and the existing medium-wave stations at Delhi, Bombay, Calcutta and Peshawar, the "All India Radio" will have in operation, 5 short-wave stations and 9 medium-wave stations. Two stations, viz., the 10 k.w. short-wave station at Delhi, and the 5 k.w. medium-wave station at Lahore, are expected to be in operation by the end of the year.

Considerable attention is paid to the development of the receivers, the present position of the broadcast receivers being considered generally unsatisfactory owing to the high cost. The Research Department of the "All India Radio" has developed receivers for use in Indian villages for community reception. "The receivers are mounted in metal cases and

padlocked. No controls appear outside the box. The receiver is left tuned to the local station. A clockwork time switch mounted in the box turns the receiver on and off at the correct time for the 'village hour', the only attention required by these receivers, is a visit once in every 3 weeks when the car accumulator batteries which operates the receiver are changed and the clock rewound."

**Marketing in India.**—At the joint Conference of the Central Marketing Staff and Senior Marketing Officers of Provinces and States, held at Simla on the 7th and 8th September, Mr. Livingstone, Chief Marketing Officer, Government of India, reviewed the progress so far made by the Marketing Staff. Since the issue of the report on wheat in April last, the Central Staff had been busy in issuing reports on rice, linseed, tobacco, grapes, cattle, eggs and milk. Twelve experimental grading and marketing stations covering eight different commodities have been started all over India.

It was decided that new marketing surveys of fish and cashew-nuts should be taken in addition to the work that would fall on the Provincial and State Marketing Staff in connection with the survey of jute, lac and cotton.

**Surveying the Himalayas.**—Remarkable work has been carried out by the Government of India Survey Department in surveying the extensive Gangotri system in the fascinating regions of the Himalayas. The area under survey includes the Utrakhund of the Hindu legend covering the five holy shrines of Jannotri, Gangotri, Kedarnath, Tunganath and Badrinath and also the peaks of Nanda Devi (25,645 ft.), Trisul (23,360 ft.), Kamet (25,447 ft.), and the Chaukamba massif (23,420 ft.). Between September 1935 and June 1936, an area 3,250 square miles were surveyed by the gallant officers of the survey (says a press note). "The Nanda Devi with its famous inner sanctuary was in the area surveyed. The Nanda Devi basin has a glaciated floor of 14,000 ft. above sea-level and is surrounded by a vast wall from 20,000 to 24,000 ft. in height, broken only at the western end of the gorge of Rishiganga. The peak of Nanda Devi rises as a vast pyramid just within the eastern rim of the basin. No human feet ever treaded the basin till Messrs. Tilman and Shipton forced their way through the gorge of the Rishiganga in 1934." A plain table survey was made of the western portion of the basin. The highest station occupied was one at 19,400 ft. Photographs were taken with a special survey camera to get the material from which an accurate survey could be made at leisure in the recess headquarters, Dehra Dun. A small area of the region still remains unsurveyed and 3 surveyers left Mussorie at the end of August to complete the work.

**Indian Central Cotton Committee.**—The Indian Central Cotton Committee has just published a Statistical Bulletin entitled "Supply and Distribution of the Various Types of Indian Cotton during the Season of 1935-36". The Bulletin deals with such important statistics as of distribution, stocks, exports, mill receipts,

etc., of Indian cotton which are classified by varieties apertaining to the season 1935-36.

There are seven appendices containing relevant statistics for past season as compared with those for 1935-36.

The statistics contained in this *Bulletin* would be of great value not only to those engaged in cotton trade and mill industry in India but also to the student of Commerce and Economics, as also to the general public to study the trend of the Indian cotton trade.

**Report of the Building Research Board for the year 1936.** (His Majesty's Stationery Office, Price 4s. Post Free 4s. 4d.).—An important feature of the Report of the Building Research Board for the year 1936 is a retrospect in which the Director of Building Research surveys the progress that has been made at the Building Research Station during the last ten years or so in the development of the applied science of building. As usual, the report contains a general review of the activities of the Board during the year and a detailed account of the numerous investigations carried out at the Building Research Station. A complete list of the publications of the Station—over 350 documents—is given in an appendix.

**Dr. Sir K. P. Puttanna Chetty** has made a donation of Rs. 20,000 to the Mysore University to form a nucleus of a fund for "bridging the gap between the University and the masses which is now too great". Those in the rural tracts feel accordingly "no pride or interest in the existence and maintenance of a University, which, rightly or wrongly they are prone to think, is interested to serve only the intellectual classes by training them in Arts and Sciences and conferring on them all the hall-marks of University Degrees. It seems that it is necessary to correct this erroneous impression and to make people in the bulk take a direct personal interest in the University, the benefits of whose work should be made to filter down to them in a manner susceptible of their easy absorption."

**Dr. Sir K. P. Puttanna Chetty** is a prominent citizen of Bangalore whose benefactions for improving the moral and material welfare of the people of the Mysore State are too well known.

*Science* reports that the Royal Society of Edinburgh has awarded the Gunning Victoria Jubilee Prize for the period 1932-36 to Prof. C. G. Darwin, Master of Christ's College, Cambridge, formerly Tait Professor of Natural Philosophy in the University of Edinburgh, for his distinguished contributions to Mathematical Physics.

**Prof. H. C. Urey**, who in collaboration with Dr. G. M. Murphy and Dr. F. G. Brickwedde discovered the heavy hydrogen, has succeeded in isolating Heavy Nitrogen. Chemists throughout the world will extend hearty congratulations to Prof. Urey for his great achievement.

**The Coate's Medal** for the year 1936, has been awarded to Dr. S. K. Mukherjee for his contribution to Ophthalmology.

**Calcutta Review** announces that the Société de Géographie Commerciale et d'Études Coloniales, Paris, has awarded the Gaudy Medal this year to Dr. S. P. Chatterjee, M.Sc., T.D., Ph.D., F.G.S., Lecturer-in-charge of Geography Teachers' Training Department of the University of Calcutta, for his work on "Le Plateau de Meghalaya". He has been invited to attend the Congrès International des Sociétés de Géographie Économique, to receive the medal.

**The Premchand Roychand Studentship** for 1936, has been equally divided between Messrs. Dineshchandra Sen, M.Sc., and Ramprasad Mitra, M.Sc. Messrs. H. K. Nandy, M.Sc., and Harischandra Roy, M.Sc., have been granted special scholarships.

**Mr. J. F. Blackiston**, Director-General of Archaeology, has retired with effect from 21st September.

**The Dust Counter.**—We have just received a leaflet of Messrs. Bausch & Lomb, Rochester, New York, describing their Dust Counter which in one compact unit contains both the sampling and counting apparatus. "More inclusive and liberal legislation with reference to occupational diseases makes the matter of dust hazards, of paramount importance. Not only is it necessary for the employer to institute protective measures but also in order to protect himself against unjust claims, he should have accurate records of actual working conditions." The Air sampling mechanism consists of a moistening chamber through which air is drawn by means of an accurate calibrated hand pump of 1/1,000 c.ft. capacity and an impinging device which deposits the dust particles suspended in the air on a circular glass plate within the instrument, in the form of a ribbon. Twelve samples may be collected on one slide. These samples may be viewed and counted at once, without removing the slide by means of a built-in compound microscope of 200× magnification with a special dark field illuminating system. The microscope is fitted with a special hyperplane eye-piece in which there is a micrometer disc ruled in 30 micron squares. These square areas are used for dust counting. An extra line is ruled along the side squares to permit approximate measurement of particles for classification according to sizes. Further details regarding the instrument can be had from Messrs. Martin & Harris, Ltd., Calcutta, who are the sole agents in India for the products of Messrs. Bausch & Lomb.

**The Holden Expedition of the American Museum of Natural History.**—An expedition led by Dr. William Ball Holden, left New York on August 21, to carry on scientific exploration in the Amazonian Jungles of South America. The main object of the expedition which is expected to take about 6 months, will be to carry out an intensive study of the diseases and drugs of the Indian Tribes which live along the northern tributaries of the Amazon River. At the same time the other members of the party will collect reptiles, amphibians, small mammals and insects, as well as botanical specimens. The



section to be explored is the little known Sierra Akarai range of mountains in the southernmost portion of British Guiana along and within the Brazilian border (*Science*, 1937, 86, 215).

# Announcements.

**Indian Central Cotton Committee.**—*Facilities for Training at the Technological Laboratory, Matunga.*—As in the past, the Technological Laboratory will admit this year two students for training in the elements of spinning and the routine methods of testing cotton fibre and yarn. The selected candidates will be expected to join on the 3rd January 1938 and will conform to the Laboratory regulations regarding hours of work, etc. The course will normally last for a period of six months and a fee of Rs. 50 only, which is not refundable, will be charged for the full course.

Candidates desirous of admission should submit written applications to the Director, Technological Laboratory, Matunga, Bombay, so as to reach him not later than 10th November 1937.

**The Eighth Annual Meeting of the Central Board of Irrigation** will be held at Delhi from October 30 to November 4. The following subjects will be considered:

- (1) Summarized reports on Irrigation research work done in India during the year 1936-37.
- (2) Subjects brought forward from last year and
- (3) The role of reservoirs in river flood control. The subjects to be investigated during the ensuing year will also be considered at the Meeting.

**The Centenary of the Invention of Pitman's Shorthand** comes off on Saturday, 20th November 1937, which will be celebrated all over the world in a suitable manner. The invention of Phonography due to the genius of Sir Isaac Pitman has been a great boon rendering speedy transaction of modern business possible.

**The Thirtieth All-India Educational Conference** will be held at Calcutta during Christmas holidays. The Conference will be held under the auspices of the All-India Federation of Educational Associations. Mr. S. K. Roy Choudhury, M.A., B.L., Mayor of Calcutta, is the Chairman of the Reception Committee and K. P. Chattopadhyay, B.Sc., M.A., the General Secretary.

**Inter-University Board.**—The Annual Meeting of the Inter-University Board of India will be held at Allahabad from 13th-15th December 1937. Among the themes for discussion at the meeting, are (1) closer co-ordination between the Indian Military Academy, Dehra Dun, and the Indian Universities in which Training Corps have been organised, (2) mutual recognition of the corresponding examinations of different universities for

purposes of eligibility of admission from one university to any other and (3) collaboration between the Government and the Universities in investigations relating to agricultural and industrial problems.

We acknowledge with thanks, receipt of the following:—

- "Journal of Agricultural Research," Vol. 55, Nos. 2 and 3.
- "Monthly Bulletin of Agricultural Science and Practice," Vol. 28, No. 9.
- "Agricultural Gazette of New South Wales," Vol. 48, No. 9.
- "Agriculture and Live-Stock in India," Vol. 7, Part 5.
- "The Philippine Agriculturist," Vol. 26, No. 4.
- "Allahabad Farmer," Vol. 11, No. 5.
- "Journal of the Royal Society of Arts," Nos. 4423-26.
- "Biochemical Journal," Vol. 31, No. 8.
- "Journal of the Institute of Brewing," Vol. 43, No. 9.
- "Chemical Age," Vol. 38, Nos. 948-51.
- "Journal of Chemical Physics," Vol. 5, No. 9.
- "Journal of the Indian Chemical Society," Vol. 14, Nos. 7-8.
- "Berichte der Deutschen Chemischen Gesellschaft," Vol. 70, No. 9.
- "Experiment Station Record," Vol. 77, Nos. 2 and 3.
- "Transactions of the Faraday Society," Vol. 33, No. 197.
- "Indian Forester," Vol. 63, No. 10.
- "Forschungen und Fortschritte," Vol. 13, Nos. 25-27.
- "Journal of the Indian Mathematical Society," Vol. 2, No. 7.
- "Marriage Hygiene," Vol. 4, No. 1.
- "Medico Surgical Suggestions," Vol. 6, No. 9.
- "Calcutta Medical Journal," Vol. 32, No. 10.
- "Journal of the American Museum of Natural History," Vol. 40, No. 2.
- "Journal of the Bombay Natural History Society," Vol. 39, No. 3.
- "Nature," Vol. 140, Nos. 3539-542.
- "Journal of Nutrition," Vol. 14, No. 3.
- "Indian Journal of Physics," Vol. 11, No. 4.
- "Research and Progress," Vol. 3, No. 5.
- "Canadian Journal of Research," Vol. 15, No. 8.
- "Science and Culture," Vol. 3, No. 3.
- "The Sky," Vol. 1, No. 11.
- "Indian Trade Journal," Vol. 126, Nos. 1629-33.
- "Indian Journal of Veterinary Science and Animal Husbandry," Vol. 7, No. 3.

# CATALOGUE.

Cambridge University Press: "Autumn Books".

## ACADEMIES AND SOCIETIES.

## Indian Academy of Sciences:

September 1937. SECTION A.—S. S. BHATNAGAR, H. LESSHEIM AND M. L. KHANNA: *The Ground State of the  $Se_2$  Molecule*.—It has been sought to decide whether the ground state is  $^3\Sigma$  or  $^1\Sigma$  from magnetic measurements on the vapour. The vapour of selenium is definitely paramagnetic. B. S. MADHAVA ROW: *Generalised Action-Functions in Born's Electro-Dynamics*. S. R. SAVUR: *The Replication of an Experiment. Part I.—Identical Samples from a Binomial Population*. S. S. PILLAI: *Generalisation of a Theorem of Davenport on the Addition of Residue Classes*. K. C. PANDYA AND T. A. VAHIDY: *The Condensation of Aldehydes with Malonic Acid in the Presence of Organic Bases. Part IX.—The Condensation of  $\beta$ -Hydroxy-naphthaldehyde (2-Hydroxy-1-naphthaldehyde)*.—Unlike the case with salicylaldehyde, the condensation here is effected very readily, even without any organic base. R. D. DESAI AND S. B. HAMID: *Heterocyclic Compounds. Part IV.—Coumarins from Resacetophenone and Ethylacetoacetate and Synthesis of Coumarino- $\gamma$ -Pyrones*.—Resacetophenone condenses with ethylacetoacetate in the presence of phosphorus oxychloride to give a coumarin from which the coumarino- $\gamma$ -pyrones can be readily obtained by the Kostanecki Reaction. S. SIDDIQUI AND V. SHARMA: *Studies in the Conessine Series. Part III.—Degradation of Conessine and Iso-Conessine Hydroxides to a Common Hydrocarbon*. R. L. MOORE: *A Combined Electrometer and Thermionic Voltmeter*.—A design is given for A. C. ranges 0–6, +0–10 volts and D.C. ranges 0–3 and 0–6 volts. S. SIDDIQUI AND V. SHARMA: *Studies in the Conessine Series. Part IV.—Action of Nitric Acid on Conessine and the Reduction of One of its Two Isomeric Mono-Nitro Derivatives to Mono-Oxy and Iso-dioxy-conessine*. R. K. ASUNDI AND Y. P. PARTI: *On the Emission and Absorption Band Spectra of Selenium*. L. SIBAIYA: *Nuclear Spin of Rhodium*.—The isotope Rh 103 has a nuclear spin of  $\frac{1}{2}$  with a small positive magnetic moment.

September 1937. SECTION B.—JAI CHAND LUTHRA AND Inder Singh CHIMA: *Some Studies of Temperature of the Cotton Plant in the Punjab*.—The temperature of the leaves follows closely the temperature of the surrounding air. Soil moisture, however, exercises a marked influence on the temperature of the leaves, the plants of the unirrigated crop showing a higher temperature of 4°–5° C. during September in the afternoon, while that of the irrigated crop was lower by 2°–3° C. A. RAMAKRISHNA REDDY: *The Physiology of Digestion and Absorption in the Crab, Paratelphusa (Oziotelphusa) hydrodromus (Herbst)*.—A detailed account of the digestive process in the common South Indian field crab. J. H. MITTER AND R. N. TANDON: *Fungi of Allahabad, India, Part III*.—The fungi listed include some which have new hosts; some which have not been recorded in *The Fungi of India* by Butler

and Bisby; fifteen species and one genus in the list are described for the first time in *Annales Mycologici-Fungi indici* by the authors.

## Indian Chemical Society:

July 1937.—HIRENDRA NATH DAS-GUPTA: *Studies in Organo-arsenic Compounds—Part VI. Synthesis of 1-Chloroarsindole from Cinnamic Acid*. HIRENDRA NATH DAS-GUPTA: *Studies in Organo-arsenic Compounds—Part VII. Synthesis of Arsindole Derivatives*. G. A. DALAL AND K. S. NARGUND: *Condensation of Succinic Anhydride with the Methyl Ethers of Dihydric Phenols*. TEJENDRA NATH GHOSH: *Quinazolines, Part I*. SUSIL KUMAR RAY: *Studies on the Formation of Dyes derived from 8-Oxyquinoline Aldehydes and from 2-Oxyanthraquinone Aldehyde*. NRIPENDRA NATH CHATTERJEE: *Terpene Compounds—Part I. Synthetic Study on the Structure of Azulene*. P. C. MITTER AND SUDHIR CHANDRA RAY: *Synthesis of Substances related to Capsaicin*. J. C. GHOSH, S. K. BHATTACHARYYA AND M. I. NARASIMHA MURTHI: *On the Photobromination of Acetylene Dichloride in the Gaseous Phase*. BALWANT SINGH AND IJAZ ILAHI MALIK: *Potentiometric Studies in Oxidation-Reduction Reactions. Part III. Reduction with Sodium Sulphite*. BHABES CHANDRA RAY: *On the Constitution of Erdmann's Salt, Part I*.

## Indian Association for the Cultivation of Science:

September 1937.—JAGANNATH GUPTA: *Free Rotation in the Oxalate Group and the Resonance Bond of Carbozyl*. B. N. BISWAS: *Derivation of the Latent Heat Equation from the Principles of Dilute Solution*. M. K. SEN: *Spin Doubling in  $2\Sigma$  States of  $AlO$* . S. C. SIKKAR AND J. GUPTA: *On the Crystal Structure of p-Dichlorobenzene at Different Temperatures*. K. PROSAD AND L. M. CHATTERJEE: *Investigations on the Release of Electrical Charges under Moderate Pressure from Photographic Plates and other Materials*.

## Society of Biological Chemists, India:

Bangalore, 11th September 1937.—SYMPOSIUM ON "CANE MOLASSES".—RAJAMANTRAPRAVINA MR. N. MADHAVA RAO, B.A., B.L.: *Opening Address*. B. T. NARAYANAN: *Molasses as a Fertilizer and Soil Reclaimant in Agriculture*. T. R. BHASKARAN AND S. C. PILLAI: *Decomposition of Cane Molasses in the Soil and its Bearing on Soil Fertility*. T. R. BHASKARAN AND S. C. PILLAI: *Utilization of Molasses for the Dissolution of Bone and Rock Phosphates*. D. A. HUKERI: *The Application of Molasses to Macadam Surface*. Y. K. RAGHUNATHA RAO: *Glycerine from Fermentation of Waste Cane Molasses*. S. RAJAGOPAL AND A. V. VARADARAJA IYENGAR: *Molasses as a Biological Starter in the Decomposition of Resistant Cellulosic Material*. G. GUNDU RAO AND M. T. N. IYENGAR: *Crystal-Molasses Ratios in Massescuties by a Conductivity Method*. S. RAJAGOPAL: *Manufacture of Yeast from Molasses*.

## ERRATUM.

Vol. VI, No. 3, September 1937, pages 101–02, contribution entitled "Sexual Organs of *Pythium arrhenomanes* Drechsler on Artificial Substrata":

For "all" occurring on page 102, column 1, line 18, read "also".

